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January 24, 2003
B-09075-0143-0502
REPA3-0502-051

Mr. Bernie Orenstein
Regional Project Officer
U.S. EPA Region 5 (DM-7J)
77 West Jackson Boulevard
Chicago, IL 60604

Subject: EPA Contract No. 68-W-02-018, Work Assignment R05802, RCRA Corrective Action, Task 02. Technical Direction No. 1.AK Steel, Middletown, Ohio, Task 04. Draft Quality Assurance Project Plan for Fish Analyses.

Dear Mr. Orenstein:

In response to Work Assignment R05802, Task 04, under EPA Contract No. 68-W-02-018, please find attached Booz Allen Hamilton's (Booz Allen's) Draft Quality Assurance Project Plan (QAPP) for retrieving the frozen fish held in the Ohio EPA freezer in Groveport, Ohio and shipping the samples to the Severn-Trent Laboratory in Knoxville, TN for analyis. The samples will be analyzed for polychlorinated biphenyls (PCB) aroclors by Method 8082, PCB congeners by Method 1668, and Dioxin/Furans by Method 1613. Once EPA has reviewed and approved this QAPP, Booz Allen will finalize the document and resubmit with the appropriate signatures.

If you have any questions regarding this deliverable, please contact me at (254) 793-3419.

Sincerely,

BOOZ ALLEN HAMILTON (for)

Phebe Davol
Work Assignment Manager

DRAFT

cc: Alan Wojtas, Work Assignment Manager
Gary Cygan, Technical Advisor
Michael Mikulka, Technical Advisor
Gloria Kane, Contracting Officer (cover letter only)
Jody Gosneil, Contract Specialist (cover letter only)
BAH EPMT QA/QC Coordinator

QUALITY ASSURANCE PROJECT PLAN

FOR
ANALYSIS OF FISH TISSUE SAMPLES

IN SUPPORT OF
U.S. ENVIRONMENTAL PROTECTION AGENCY REGION 5

UNDER
RCRA ENFORCEMENT, PERMITTING, AND ASSISTANCE (REPA3)
ZONE 2–REGION 5

DOCUMENT CONTROL NUMBER
REPA3-0502-051

REVISION NO. 0
EFFECTIVE DATE: 22 JANUARY 2003

DRAFT

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AK5 041841

INTRODUCTION

Under the Environmental Protection Agency (EPA) RCRA Enforcement, Permitting, and Assistance (REPA3) Contract, Work Assignment R05802, Booz Allen Hamilton (Booz Allen) has been tasked to coordinate the analysis of samples of fish tissue collected from a site in Ohio. This site-specific Quality Assurance Project Plan (QAPP) has been prepared to document procedures and methods to be used during fish tissue sample analysis.

Detailed information about Booz Allen's quality assurance (QA) and quality control (QC) protocols for sampling and analysis activities in Region 5 is presented in the Booz Allen Region 5 Quality Assurance Project Plan (R5 QAPP). This site-specific QAPP will not duplicate information provided in this Regional QAPP; it will supplement the plan with information that is specific to this project. Both this site-specific QAPP and the R5 QAPP are subordinate to and consistent with the REPA3 Quality Management Plan (QMP). In this manner, Booz Allen provides a comprehensive and consistent environmental QA/QC program with sufficient flexibility to meet the particular requirements of Region 5 and the circumstances of each project.

The REPA3 QMP establishes Booz Allen's quality system for all REPA3 work assignments. It outlines our corporate quality policy and describes the overall organization and general approach to quality management for these contracts. The QMP also defines requirements for control of accountable documents and records, provides the strategy for assessing the effectiveness and implementation of the overall quality system, describes the roles of and interrelationships between the various QA/QC plans, and describes how the quality of subcontracted work will be controlled.

This QAPP is a sub-tier document to the Booz Allen R5 QAPP, which outlines the general requirements and protocols for environmental sampling and analysis activities performed under REPA3 in EPA Region 5. The R5 QAPP was designed to be compliant with and support the Region's quality management policies as prescribed in *RCRA QAPP Instructions U.S. EPA Region 5*, Revision April 1998. It was also designed to be consistent with *EPA Requirements for Quality Assurance Project Plans* (QA/R-5), *EPA Guidance for Quality Assurance Project Plans* (QA/G-5), *EPA Quality Manual for Environmental Programs (EPA 5360)*, and *Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs* (ANSI/ASQC E4-1994). In conjunction with each work assignment statement of work (SOW), the R5 QAPP provides guidance and requirements for developing and implementing site QAPPs that are also compliant with these reference documents. In the event of conflicting requirements, the order of precedence will be the contract SOW, this site-specific QAPP, the R5 QAPP, and the QMP. All of these documents will take precedence over previously existing QAPPs or standard operating procedures (SOP).

ELEMENT 1: TITLE/SIGNATURE PAGE

The following persons approve the contents of this *Quality Assurance Project Plan for Analysis of Fish Tissue Samples* and are committed to implementing the provisions described herein:

Yvonne Fernandez (signature/date)
Booz Allen Hamilton PQAM

Robert Springer (signature/date)
EPA Region 5 REPA3 PQAM

Phebe Davol (signature/date)
Booz Allen Hamilton WAM

Alan Wojtas (signature/date)
EPA Region 5 WAM

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ELEMENT 2: TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF APPENDICES

DISTRIBUTION

Booz Allen Region 5 Regional Manager
Booz Allen Region 5 WAM

EPA Region 5 Project Officer
EPA Region 5 WAM
EPA Region 5 QA Coordinator

ELEMENT 3: PROJECT DESCRIPTION

3.1 GENERAL REQUIREMENTS

EPA Region 5 has tasked Booz Allen Hamilton (Booz Allen) to coordinate analysis of fish tissue samples for the following:

- Polychlorinated biphenyls (PCB) congeners via high resolution gas chromatography/mass spectrometry (HRGC/HRMS): Method 1668,
- PCB Aroclors by gas chromatography (GC): Method 8082, and
- Dioxins/furans, including 17 congeners by HRGC/HRMS: Method 1613

The analyses will be conducted to determine a toxicity-weighted total concentration for each sample, considering both dioxin-like PCBs as well as dioxins/furans.

3.2 SITE DESCRIPTION

The Ohio EPA collected samples of fish tissue on July 20, 2002. Samples were collected at three locations, in accordance with an Ohio EPA Sampling Plan. Once the fish were collected, they were identified, weighed and measured, then cleaned in accordance with Ohio EPA protocols. Upon cleaning, each individual fish (where only 1 fish was collected at that station), or two fish (where 2 fish in a similar size class were collected), were bagged and frozen for later analysis.

3.3 SITE HISTORY AND BACKGROUND

Sediment sampling has shown the sediments at this site are contaminated with PCBs. Past fish tissue analyses by Ohio EPA and others have shown that the fish collected at this site are also contaminated with PCBs.

3.4 PROJECT OBJECTIVES

The objective of the project is to determine a toxicity-weighted total concentration for each sample, considering both dioxin-like PCBs aroclors and congeners, as well as dioxins/furans.

Past analytical work by Ohio EPA has been limited to PCB aroclors. Metabolic action on the PCBs by the fish may have resulted in changes to the PCB patterns in the tissue such that the original Aroclor pattern is no longer present. In addition, bioaccumulated PCBs may be more toxic and more persistent than the original aroclor mixtures. Therefore, specific PCB congener testing is appropriate to ascertain the true nature of the PCBs present in the fish, and hence to develop a more accurate assessment of the risks from fish consumption from the site on human health.

Upon receipt of the analytical data, U.S. EPA will use the information identified in Table 5-7 of the *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1, Fish Sampling and Analysis, Third Edition, U.S. EPA Report EPA 823-B-00-007, dated*

November 2002, as the basis to determine the total toxicity of the tetra- through octa-chlorinated dibenzo-p-dioxins and dibenzofurans and dioxin-like PCBs in this study.

3.5 TARGET PARAMETER LIST

Fish tissue samples will be analyzed for the following:

- PCB congeners via HRGC/HRMS: Method 1668
- PCB Aroclors by GC: Method 8082
- Dioxins/furans (17 congeners) by HRGC/HRMS: Method 1613

Analyses will include as many of the 209 PCB congeners as possible (about 120 under HRMS). Analyte lists for each of the methods are provided in the laboratory SOPs in Appendices A, B, and C.

In addition to the above analyses, a lipid analysis by a gravimetric method will also be performed and reported (as percent lipid by wet weight) for each composite or individual fish sample. Section 2.1.4 in the laboratory SOP for Method 1668 contains the reference for the percent lipids determination.

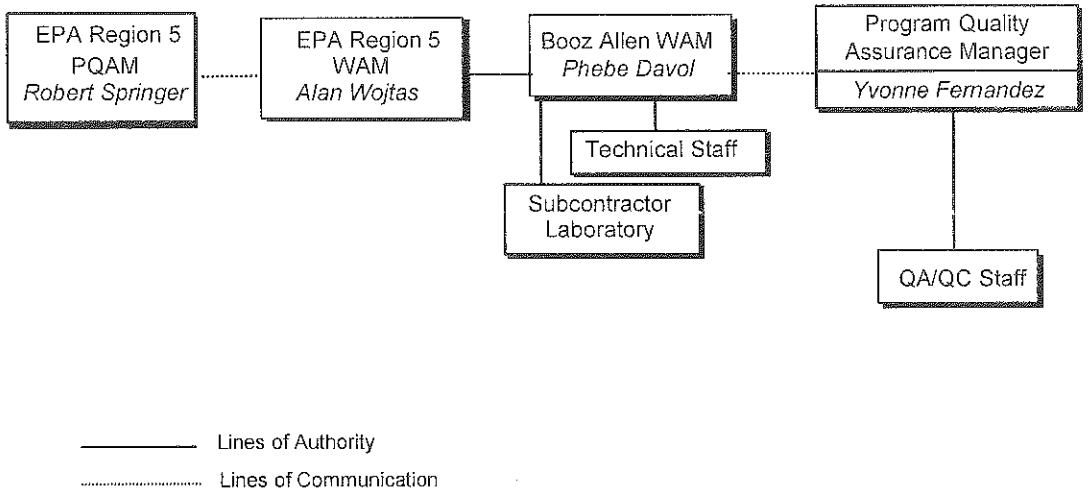
3.6 RISK-RELATED ISSUES

This section is not applicable to this project.

ELEMENT 4: PROJECT ORGANIZATION AND RESPONSIBILITY

This section identifies the individuals and organizations responsible for the planning and execution of field operations to be performed under this QAPP. The project organization is depicted in Figure 4-1. The REPA3 QMP and R5 QAPP provide a full description of all program-level functions.

Figure 4-1. REPA3 Organization for Project Support



4.1 SPECIAL TRAINING/CERTIFICATION

Project personnel will be trained and certified as prescribed in the Booz Allen QMP. The technical staff will be provided with and required to read the work assignment, work plan, QMP, R5 QAPP, site QAPP, and SOPs. Each member of the technical staff must demonstrate proficiency with their assigned duties to include the preparation of associated documentation.

ELEMENT 5: QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

5.1 PROJECT-SPECIFIC QA OBJECTIVES

Tables 5-1 through 5-3 below present reporting limits and minimum levels (ML) for the methods proposed for this project. SOPs for the analytical methods are included in Appendix A.

5.1.1 Reporting Limits for PCB Aroclors by Method 8082

Reporting limits for PCB aroclors are shown in Table 5-1 below.

Table 5-1. Reporting Limits for Method SW8082

PARAMETER/METHOD	ANALYTE	SOLID	
		RL	UNIT
PCBs	PCB-1016	33	µg/kg
SW8082	PCB-1221	33	µg/kg
	PCB-1232	33	µg/kg
	PCB-1242	33	µg/kg
	PCB-1248	33	µg/kg
	PCB-1254	33	µg/kg
	PCB-1260	33	µg/kg

5.1.2 Reporting Limits for PCB Congeners by Method 1668

STL Knoxville's Specialty Organics Group reports results for all 209 congeners by Method 1668A. The method does not provide for the chromatographic resolution of each congener, but does uniquely resolve approximately 140 congeners, depending upon the performance of the individual chromatographic column. STL Knoxville provides results for all results for all chromatographic peaks that are at least 2.5 times the intensity of the background noise. Results falling below the Estimated Minimum Level are qualified with a J flag. The Estimated Detection Limit (EDL) appears in the Detection Limit field for all analytes. When no peak is detected above the 2.5 signal-to-noise level, "ND" appears in the result column, and the EDL is placed in the Detection Limit field.

Table 5-2 below presents the estimated minimum levels for Method 1668.

Table 5-2. Estimated Minimum Levels (ML) for Method 1668

PARAMETER/METHOD	ANALYTE	SOLID (10 g)	
		EML	UNIT
PCBs	Monochlorobiphenyls	0.025	ng/g
1668	Dichlorobiphenyls	0.025	ng/g
	Trichlorobiphenyls	0.025	ng/g
	Tetrachlorobiphenyls	0.025	ng/g
	Pentachlorobiphenyls	0.025	ng/g
	Hexachlorobiphenyls	0.025	ng/g
	Heptachlorobiphenyls	0.025	ng/g
	Octachlorobiphenyls	0.025	ng/g

PARAMETER/METHOD	ANALYTE	SOLID (10 g)	
		EML	UNIT
	Nonachlorobiphenyls	0.025	ng/g
	Decachlorobiphenyl	0.025	ng/g

The estimated minimum level (EML) is defined as the lowest concentration at which an analyte can be measured reliably with common laboratory interferences present assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures. Deviations from the extraction amounts or final volumes listed will result in corresponding changes in the actual sample EML.

These EMLs differ from those listed in the reference method. The EMLs provided are based on historical blank data and calibration data obtained while performing EPA 1668mod. The survey period was approximately 2 years. During this period, blank contamination in excess of the minimum levels was rare. These EMLs are half the average EML reported in the method.

5.1.3 Reporting Limits for Dioxins/Furans by Method 1613

Reporting limits for dioxins/furans by Method 1613 are shown in Table 5-3 below.

Table 5-3. Minimum Levels (ML) for Method 1613B
Dioxins/Furans by HR GC/HRMS

PARAMETER/METHOD	ANALYTE	TISSUE	
		MCL	UNIT
Dioxins/Furans	2,3,7,8-TCDD	1.0	pg/g
1613	1,2,3,7,8-PeCDD	5.0	pg/g
	1,2,3,4,7,8-HxCDD	5.0	pg/g
	1,2,3,6,7,8-HxCDD	5.0	pg/g
	1,2,3,7,8,9-HxCDD	5.0	pg/g
	1,2,3,4,6,7,8-HPCDD	5.0	pg/g
	OCDD	10	pg/g
	2,3,7,8-TCDF	1.0	pg/g
	1,2,3,7,8-PECDF	5.0	pg/g
	2,3,4,7,8-PECDF	5.0	pg/g
	1,2,3,4,7,8-HXCDF	5.0	pg/g
	1,2,3,6,7,8-HXCDF	5.0	pg/g
	2,3,4,6,7,8-HXCDF	5.0	pg/g
	1,2,3,7,8,9-HXCDF	5.0	pg/g
	1,2,3,4,6,7,8-HPCDF	5.0	pg/g
	1,2,3,4,7,8,9-HPCDF	5.0	pg/g
	OCDF	10	pg/g

Method 1613 is very similar to the CLP method DLM01.4 and SW-846 Method 8290. Both methods reference the ML. The qualitative definition of the ML is "the lowest level at which the analytical system must give a reliable signal and an acceptable calibration point". The ML was introduced in EPA Methods 1624 and 1625 in 1980 and was promulgated in these methods in 1984 at 40 CFR Part 136, Appendix A.

The USEPA Engineering and Assessment Division has established guidance for setting the ML which is a level set 2 to 3 times the interlaboratory method detection limits (MDL) established for the methods during validation. Unlike the way 40 CFR Part 136A is often used (i.e., as a measure of individual laboratory performance) the MLs established for 8290 and 1613 were established from data at multiple laboratories to assess method performance.

The lab will report all detections down to the smallest allowable peaks (i.e., 2.5 times the average noise for three consecutive scans). The Estimated Detection Limit (EDL) is also provided for each analyte. The EDL is a value calculated to estimate the concentration in the sample that would meet the minimum signal-to-noise requirement (2.5 times the intensity of the average noise level). The EDL does not exactly equal the smallest amount reported. This is primarily due to differences in the way the two values are calculated. The EDL is calculated using peak intensity, whereas the sample concentration is calculated on the basis of area. The ratio between the two varies with concentration. Any detections below the ML are qualified by a J flag.

5.1.4 Estimated Detection Limits

If no peaks are present in the region of the ion chromatogram where the compounds of interest are expected to elute, the EDL for that compound is calculated and reported. The EDL reflects the amount of the particular analyte that would be required to cause a positive result for the particular analysis.

The EDL is calculated according to the following equation:

$$\text{Estimated Detection Limit} = \frac{N \times 2.5 \times Qis}{His \times RRF \times W \times S}$$

where:

N = peak to peak noise of quantitation ion signal in the region of the ion chromatogram where the compound of interest is expected to elute
His = peak height of quantitation ion for appropriate internal standard
Qis = ng of internal standard added to sample
RRF = mean relative response factor of compound obtained during initial calibration
W = amount of sample extracted (grams or liters)
S = percent solids (optional, if results are requested to be reported on dry weight basis)

5.2 ANALYTICAL QA OBJECTIVES

All analyses will be performed in accordance with method requirements, as described in the attached laboratory SOPs in Appendices A, B, and C. Appropriate calibrations, blanks, and performance tests will be performed as specified in these SOPs. Acceptance criteria for Method 1613 are found in Tables 9 and 10 of the laboratory's SOP for Method 1613 (Appendix C). Acceptance criteria for Method 1668 are found in Table 10 of the laboratory's SOP for Method 1668 (Appendix B). Acceptance criteria for Method 8082 are found in Table 5-4 below.

Table 5-4. Quality Control Acceptance Criteria for Method SW8082

METHOD	ANALYTE	ACCURACY SOLID (% R)	PRECISION SOLID (% RPD)
SW8082	PCB-1016	44–127	≤ 50
	PCB-1221	31–136	≤ 50
	PCB-1232	31–136	≤ 50
	PCB-1242	29–160	≤ 50
	PCB-1248	31–136	≤ 50
	PCB-1254	25–141	≤ 50
	PCB-1260	31–136	≤ 50
	Surrogate:		
	DCBP	25–143	

5.3 NON-DIRECT MEASUREMENTS

Non-direct measurements will not be required for this project.

ELEMENT 6: SAMPLING PROCEDURES

6.1 SAMPLING METHODS

The required samples of fish tissue were collected by the Ohio EPA on July 20, 2002. Samples were collected using electrofishing wading methods at three locations, in accordance with an Ohio EPA Sampling Plan. Once the fish were collected, they were identified, weighed and measured, then filleted in accordance with Ohio EPA protocols. Each filleted sample was wrapped in aluminum foil, placed in a sealed plastic bag, and frozen at –20 °C for later analysis.

The laboratory to be used should prepare the samples for analysis consistent with Section 7 of the *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1, Fish Sampling and Analysis, Third Edition, U.S. EPA Report EPA 823-B-00-007, November 2002.*

Sample container and preservative requirements are listed in Table 6-1. The laboratory should follow the procedures specified in their SOPs during analyses of the samples.

Table 6-1. Sample Preservation, Containers, and Holding Times

NAME	ANALYTICAL METHOD	CONTAINER	PRESERVATION	MINIMUM SAMPLE VOLUME OR WEIGHT	MAXIMUM HOLDING TIME
PCBs	SW8082 (s)	Not specified	-10 C before extraction, -6 C after extraction	8 oz.	1 year until extraction and 40 days after extraction
PCB Congeners (including PCB-81)	1668	Not specified	-10 C	8 oz.	1 year until extraction
Dioxins and furans (PCDD/PCDF)	1613B SW8290	Not specified	-10 C	8 oz.	1 year until extraction

6.2 FIELD QC SAMPLES

One duplicate fish tissue sample will be submitted to the laboratory. Results will be used to measure the variability in sample collection and analysis.

6.3 SAMPLE CONTAINERS

The samples were collected on July 20, 2002. Upon collection, each fish was filleted, and the filleted sample was wrapped in aluminum foil, placed in a sealed plastic bag, and frozen at –20 °C for later analysis. The samples are currently being held in a chest freezer at the Ohio EPA field facility located in Groveport, Ohio. The holding time for frozen tissue samples is 1 year. If

the samples are to be stored further at the laboratory prior to analysis, the samples must be stored in borosilicate glass, polytetrafluoroethylene (PTFE), quartz, or aluminum foil. Polypropylene and polyethylene (plastic) surfaces, implements, gloves and containers are a potential source of organic contamination and should not be used unless the laboratory can clearly document they are not a source of contamination.

All sample containers and coolers to be used by the laboratory will be inspected before each use. Sample containers will be selected, prepared, cleaned, and controlled per EPA Office of Solid Waste and Emergency Response (OSWER) Directive #9240.0-05A *Specifications and Guidance for Contaminant-Free Sample Containers* (EPA 540/R-93/051, December 1992).

ELEMENT 7: CUSTODY PROCEDURES

7.1 SAMPLE IDENTIFICATION

Each sample will be assigned a unique and sequential sample number. The fish tissue samples will be numbered sequentially using the following scheme: FT-001, FT-002, etc. The sample number will be included on the sample label and referenced on the chain of custody form and all data reports related to the sample.

A label will be affixed on each fish tissue sample prior to shipment to the laboratory. Information on the sampling labels will include the sample identification number, sampler's name or initials, chemical/physical preservative used, analysis requested, date/time collected, and type of sample.

7.2 SAMPLE DELIVERY

John Reynolds of Severn Trent will be the POC for both normal business hours and for emergency situations during off-hours. Mr. Reynolds will also serve as sample custodian. The address of the laboratory and laboratory POC is listed below.

John Reynolds
STL Knoxville
5815 Middlebrook Pike
Knoxville, TN 37921
865-291-3000

7.3 SCHEDULING

Samples were collected from the site on July 20, 2002. The Booz Allen WAM, Phebe Davol, will coordinate the scheduling of sample shipment with the laboratory POCs so as to minimize sample transport and holding time.

7.4 SAMPLE CUSTODY

Custody procedures will be implemented such that accurate and complete records of sample collection, transfer of samples between personnel, sample shipment, and receipt by the laboratory are generated and retained. Samples will be handled and managed as prescribed in REPA SOP T-17: *Sample Management Procedures.* The completed chain-of-custody forms will accompany the samples to the laboratory. Ohio EPA will be responsible for shipping the samples under proper chain-of-custody procedures. Once samples have been delivered, the laboratory will maintain custody.

7.6 SAMPLE DISPOSITION

The laboratory is responsible for the proper disposal of all samples and extracts.

7.6 SHIPPING

Samples are currently being held in a chest freezer at the Ohio EPA field facility located in Groveport, Ohio. The freezer is kept at -20°C. A Booz Allen representative will travel to the Ohio EPA facility in Groveport to package and ship the samples to the subcontractor laboratory (Severn Trent) located in Knoxville, Tennessee. The samples will be shipped on dry ice so that the temperature of the samples remains at -20°C.

Samples will be shipped using Federal Express priority overnight service. Federal Express drop off locations are found at:

41 South High Street
Columbus, OH 43215 or

2850 International Street
Columbus, OH 43228

7.7 DOCUMENTS AND RECORDS

Project documents and records will be prepared or generated, reviewed, approved, and controlled as prescribed in Section 2.5 of the QMP and in accordance with EPA direction. In the event that electronic information is transferred to EPA, it will be performed in accordance with the applicable Region 5 guidelines and protocols. Analytical data reports will be the prepared by the laboratory.

7.8 FINAL EVIDENCE FILES

The final evidence file will include the REPA deliverables and analytical data reports. The Booz Allen WAM will retain these files until project closeout. At project closeout, Booz Allen will provide EPA with a list of the materials in the file and return to EPA copies of any and all documents requested from the list. The remaining materials will be packaged and shipped to the Booz Allen offices in McLean, VA for archiving in accordance with the established protocols for the REPA3 contract.

ELEMENT 8: CALIBRATION PROCEDURES AND FREQUENCY

Calibration procedures are specified in each of the analytical methods. All analytes reported will be present in the initial and continuing calibrations, and these calibrations will meet the acceptance criteria specified in Section 5 of this QAPP. Reported results will fall within the calibration range. Records of standard preparation and instrument calibration will be maintained. Records will unambiguously trace the preparation of standards and their use in calibration and quantitation of sample results. Calibration standards will be traceable to standard materials. Traceability to the National Institute of Standards and Technology (NIST) and EPA standards will be maintained to the maximum extent possible, but the source of calibration will be documented in all cases.

8.1 STANDARDS PREPARATION AND TRACEABILITY

Traceability of standards will be accomplished by comparing in-house standards to EPA or NIST materials, and by maintaining the required records. Whenever a standard is prepared, the manufacturer's lot number, the starting materials, the starting amount and volume, the source and volume of the solvent or acid, the date of preparation, and the initials of the technician will be recorded in a permanent, bound notebook. The accuracy of the standards will be established by comparison to previously prepared standards and by comparison to standards prepared independently from different starting materials.

8.2 PREPARATION OF SPIKED SAMPLES

The method used to prepare spiked samples will be documented, and the solutions used in sample preparation must be NIST traceable and current, to the maximum extent possible. For many target compounds, however, traceability to NIST may not be possible. Traceability to EPA standards or other nationally recognized standards will be used instead. In such cases, the laboratory manager will consult with the PQAM before preparing the spiked samples.

8.3 FIELD CALIBRATIONS

This section is not applicable.

8.4 LABORATORY CALIBRATIONS

Instrument calibration is a QC measure taken to verify selectivity and sensitivity. The laboratory (Severn Trent) will perform calibrations through the use of reference materials that are NIST-traceable or, if NIST-traceable materials are not available, certified from government agencies or reliable vendors. In general, analytical instruments are calibrated prior to use with standard solutions at levels appropriate for the analysis. This initial calibration is verified at the beginning of each analytical sequence and at specified intervals throughout the analytical sequence. If the initial calibration or any of the subsequent calibration verification checks fail the pre-defined acceptance criteria, the system is recalibrated. Only results generated under acceptable calibration conditions are reported. Specific calibration procedures are documented in the laboratory's SOP for each method of analysis.

ELEMENT 9: ANALYTICAL PROCEDURES

Section 9 provides routine analytical requirements and procedures that will be implemented for this project.

9.1 ANALYTICAL PARAMETERS

Proposed analytical parameters and matrices are summarized in Table 9-1 below.

Table 9-1. Analytical Parameters

ANALYTICAL METHOD	PARAMETER	Matrix
1668	PCB congeners	Fish tissue
8082	PCB aroclors	Fish tissue
1613	Dioxins/furans	Fish tissue

The laboratory responsible for the analyses above is Severn Trent, located at in Knoxville, TN.

9.2 SAMPLE PREPARATION AND ANALYSIS METHODS

The laboratory to be used should prepare the samples for analysis consistent with Section 7 of the *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Volume 1, Fish Sampling and Analysis, Third Edition, U.S. EPA Report EPA 823-B-00-007, November 2002.*

The sample preparation and analysis methods are listed in Table 9-2. Preparation and analysis methods for Methods 1668 and 1613 are contained in the laboratory SOPs in Appendices A and C of this QAPP.

Table 9-2. Sample Preparation and Analysis Methods

ANALYTICAL METHOD	PARAMETER	PREPARATORY METHODS
1668	PCB congeners	See analytical method
8082	PCB aroclors	3510C, 3520C, 3540C, 3541
1613	Dioxins/furans	See analytical method

9.3 CONFIRMATORY ANALYSIS AND METHOD VALIDATION STUDIES

In the event that a non-standard detector is used for confirmatory analysis, the site QAPP will indicate this variance and include the procedures for this analysis. Similarly, if a method validation study is required for the use of a non-standard method, then the site QAPP will indicate this as a variance to this Regional QAPP and include the rationale for using the non-standard method, and the criteria for acceptance, rejection, or qualification of the resulting data. In general, a method validation study is required any time a method is modified, is used to

determine non-standard analytes, or is used to report lower detection levels for human health or ecological risk purposes.

9.4 ANALYTICAL ISSUES

This section is not applicable to this project.

9.5 QC SAMPLES

One duplicate fish tissue sample will be submitted to the laboratory. Results will be used to measure the variability in sample collection and analysis.

ELEMENT 10: INTERNAL QUALITY CONTROL CHECKS

This section describes routine QC procedures anticipated to be employed under the REPA3 contract.

10.1 FIELD QC CHECKS

This section is not applicable to this project.

10.2 LABORATORY QC CHECKS

Laboratory QC samples (e.g., blanks and laboratory control samples) will be included in the preparation batch with the field samples as prescribed in the cited method. An analytical batch is a number of samples (not to exceed 20 environmental samples plus the associated laboratory QC samples) that are similar in composition (matrix) and that are extracted or digested at the same time and with the same lot of reagents. MSs and MSDs count as environmental samples. The term analytical batch also extends to cover samples that do not need separate extraction or digestion (e.g., volatile analyses by purge and trap). The identity of each analytical batch will be unambiguously reported with the analyses so that a reviewer can identify the QC samples and the associated environmental samples.

10.3 INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

Materials used in the execution of work will be appropriate and approved for intended uses. The procurement and handling of quality-affecting materials will be controlled to ensure initial and continued conformance with applicable technical requirements and acceptance criteria. These items will be visually inspected before shipment to the field and again before use. Inspection elements will include, as appropriate, a review of physical condition, expiration dates, limitations of use, size and quantity, and quality grade (e.g., reagents and solvents). Quality-affecting materials that are to be controlled include, but are not limited to, sample bottles, deionized water, calibration standards for field equipment, sample preservatives, disposable sampling supplies, disposable personal protective equipment (PPE), and electronic data storage media. Materials that do not meet performance specifications will be segregated and labeled to preclude use.

ELEMENT 11: DATA REDUCTION, VALIDATION, AND REPORTING

Booz Allen chemists will validate project data as outlined in REPA3 SOP M-11: *Data Validation,* the EPA National Functional Guidelines, EPA QA/G-9, and applicable Region 5 protocols. Booz Allen will perform a full data validation (100%) of project data

11.1 DATA REVIEW, VALIDATION, AND VERIFICATION

The quality and usability of environmental data that are generated or procured under REPA3 Region 5 projects will be assessed and documented as prescribed in the QMP and herein. The quality of data will be assessed to establish usability for their intended purpose and to foster continuous improvement in data collection efforts by identifying major or recurring sources of error. Data quality assessment will include data review, verification of contract compliance and attainment of DQOs, data validation, and determination of data usability.

For the purposes of this plan and any plan developed through its use, data review is defined as the process whereby the technical merit of data is determined by the organization that generates the data. During this process, achieved QC results are compared to method-specified criteria to determine whether the analyses were performed under controlled conditions. Because data review criteria are based on the analytical methods used to generate the data, the review process and results are independent of the intended use of the data. Before submitting data, each subcontract laboratory is responsible for reviewing their data, implementing corrective actions where possible, and reporting nonconformances and the corresponding corrective actions, as applicable. Field crews will review their data and implement any necessary corrective actions before submitting the data for use.

For the purposes of this plan and any plan developed through its use, data validation is defined as the independent verification of the quality and integrity of environmental data. During this process, data deliverables will be evaluated as follows: (1) contract compliance is determined; (2) data traceability is verified from raw data to custody documentation to reporting forms; (3) calculations and transcriptions are checked, (4) QC results are evaluated against procurement specifications and the applicable project DQOs, and (5) data are qualified as necessary to denote limitations on usability.

11.1.1 Data Flow and Checking

The analytical protocols provide detailed instructions and equations for calculating analyte concentrations.

The analyst performing the assay will review all results with respect to QC requirements. Compiled results will be further reviewed by at least one other qualified individual at the laboratory, with respect to completeness of the data package and compliance with all contractual and in-house QC requirements. The Booz Allen WAM or his/her designee will provide a final independent review of the completed data package with respect to contract compliance and data usability.

11.1.2 Project-Specific Requirements

Analytical results will be communicated directly from the laboratory to Booz Allen, and then only to the EPA WAM. In no case will reports, results, or data be released to a third party without prior written permission from the EPA WAM. Disk deliverable data will be prepared whenever possible by direct electronic transfer from analytical instruments to avoid transcription errors.

11.1.3 Reporting the Results of Analyses

Data will be supplied in both electronic and hardcopy media. Both reports will consist essentially of a listing specifying the client ID number, the internal laboratory ID number, the sample date, the data prepared and/or analyzed, the method, the matrix, the parameter(s) and the measured concentration(s), units, and the detection limit. QC sample results will be reported in similar format with cross-references to unambiguously relate QC results to their associated environmental samples.

11.1.4 Case File Maintenance and Record Turnover

Booz Allen and the laboratory will maintain requirements for case file maintenance and archiving. The case file will contain the following:

- Internal laboratory chain of custody
- Copy of field sample collection crew's chain of custody
- Logbook records (sample preparation, standard preparation, run sequence logs)
- Copies of final internal (laboratory) raw summary sheets from which data are entered
- Information needed to evaluate results (acceptance limits, control charts, detection limits, retention time windows, tunes, percent moisture, corrective actions)
- Instrument printouts, including chromatograms (GC, GC/MS, LC, IC, spectra of raw responses)
- Internal (laboratory) detail documentation supporting internal QA and assessment, precision, and accuracy (replicates, duplicates, matrix spikes, matrix spike duplicates, trip blanks, control samples, calibration checks).

In summary, documentation must be sufficient to recheck and recalculate reported results at a later date if it becomes necessary.

Both electronic and hardcopy data reports will be archived at the laboratory for 3 years after termination or expiration of the REPA3 contract. At that time, Booz Allen, EPA, or an EPA designee will take possession of the reports, or give the laboratory permission to destroy them. The reports will be protected from damage from moisture and fire while in the storage area. It is

recommended that records be maintained in 2-hour rated Class B file containers, meeting the requirements of NFPA 232-1975.

Case files must contain sufficient information to recalculate reported results should the need arise at a later date. Case files will be maintained for a minimum of 3 years, subject to EPA's requirements, and will be open for inspection by cognizant Booz Allen project staff. Reports will be prepared in a suitable electronic database media agreed upon between Booz Allen, the EPA WAM, and the laboratory manager, for rapid transmission among the concerned parties. In all cases, hardcopy printouts will supplement these electronic reports.

11.1.5 Detection Limits and Reporting

The MDL is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. The laboratory will establish MDLs for each method, matrix, and analyte for each instrument the laboratory plans to use for the project according to the procedures in 40 CFR 136, Appendix B. The laboratory will revalidate these MDLs at least once per 12-month period. Results less than or equal to the MDL will be reported as the MDL value and flagged.

11.1.6 Notification of Lost Samples, Reporting Error, Out-of-Control Samples, or Loss of Capability

Booz Allen will notify the EPA WAM of nonconforming conditions that may potentially impact the quality or timeliness of analysis. At the same time, proposed corrective actions will be presented. Nonconforming conditions would include out-of-control results or supporting documentation, inadvertently destroyed or lost samples, or the loss of a laboratory capability that may adversely affect analytical test results.

11.2 VERIFICATION AND VALIDATION METHODS

Data reduction, validation, verification, and archiving for the REPA3 contract will be performed as prescribed herein. REPA3-generated data will be evaluated as outlined in EPA's *National Functional Guidelines for Organic* (EPA 540/R-99/008) *and Chlorinated Dioxin/Furan* (EPA 540-R-02-003) *Data Review*, as appropriate and applicable to the methods in this QAPP.

The laboratory will apply the appropriate data qualifiers if acceptance criteria are not met and corrective action is either not successful or not performed. Booz Allen data validation chemists will review the entire data report package, determine if the data quality objectives have been met, and calculate the data completeness for the project. In addition, all or a percentage (typically 10 percent) of the data will be validated either by Booz Allen or a third-party data validation service. These results will be included in the data package deliverable sent to the EPA.

Data quality will be assessed through full validation (all criteria/all data points).

11.3 RECONCILIATION WITH USER REQUIREMENTS

After validation, the suitability of environmental data for their intended use(s) will be determined using the EPA Data Quality Assessment (DQA) process, as outlined in EPA's *Guidance for Data Quality Assessment, Practical Methods for Data Analysis*, EPA QA/G-9.

DQA is the scientific and statistical evaluation of data to determine if data obtained from environmental data operations are of the right type, quality, and quantity to support their intended use. By implementing the DQA process, the user can determine (1) if the decision can be made with the desired confidence, given the quality of the data, and (2) how well the sampling design can be expected to perform if repeated under the same or similar circumstances.

DQA involves five steps that begin with a review of the planning or scoping documentation and end with an answer to the question posed during the planning phase of the study. A team of reviewers, who generally include chemists, statisticians, and other applicable technical personnel (e.g., risk assessor and hydrogeologist), will implement DQA as an iterative process. The five steps, which are described in detail in EPA QA/G-9, are summarized briefly as follows:

- Review the DQOs and sampling design—The review team assesses DQO outputs to ensure that they are still applicable. If DQOs have not been developed, DQOs must be specified before evaluating the data. The sampling design and data collection documentation are then reviewed for consistency with the DQOs.
- Conduct a preliminary data review—The review team assesses QA reports, calculates basic statistics, and generates graphs of the data. This information is then used to gain a better understanding about the structure of the data and identify patterns, relationships, or potential anomalies.
- Select a statistical test—The review team selects the most appropriate procedure for summarizing and analyzing the data, based on the review of the DQOs, the sampling design, and the preliminary data evaluation. The review team also identifies the key underlying assumptions that must hold true for the statistical procedures to be valid.
- Verify the assumptions of the statistical tool—The review team determines if the underlying assumptions hold true or if the departures are acceptable, given the actual data and other information about the study.
- Draw conclusions from the data—The review team performs the calculations required for the statistical test and documents the inferences that result from these calculations. If there is potential that the sampling design may be used again, the review team evaluates the effectiveness of the sampling design.

In conjunction with the process outlined in EPA QA/G-9, usability will be assessed in accordance with the applicable EPA guidance. For example, data usability for the purposes of risk assessments is generally determined as prescribed in EPA's *Guidance for Data Usability in*

Risk Assessment, (OSWER 9285.7-09). If required, non-standard techniques or criteria will be documented in the site QAPP.

ELEMENT 12: PERFORMANCE AND SYSTEM AUDITS

Booz Allen's overall assessment program is described in the REPA3 QMP. Section 4 of the R5 QAPP supplements the requirements of the QMP and further addresses the assessment tools that are most relevant and specific to environmental sampling and analysis: technical systems audits (TSA) of sampling systems, analytical and testing systems, and data management and validation systems. TSAs will be used to verify the effectiveness of and compliance with the REPA3 QMP and R5 QAPP.

Prior to implementation of field activities, internal readiness reviews are conducted by Booz Allen to verify that work prerequisites have been satisfied. The readiness review provides a systematic process for assessing, verifying, and ensuring the readiness of the project team to proceed with field activities, such soil sampling. The focus of the readiness review is to ensure that technical and quality procedures have been reviewed for adequacy and appropriateness and approved for implementation; personnel are suitably qualified for the work; and the proper equipment, materials, and resources are identified and available. The readiness review specifically addresses readiness issues at the following stages of project planning and execution: (a) during the later stages of project planning (before deployment), (b) at the beginning stages of field work (after deployment), and (c) before resuming field work after a quality-mandated stop work order is lifted or after a prolonged period of stop work due to other causes.

ELEMENT 13: PREVENTIVE MAINTENANCE

Laboratory equipment will be appropriate and approved for intended uses. Detailed information regarding preventive maintenance procedures is included in the R5 QAPP.

ELEMENT 14: SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA QUALITY

This element addresses the procedures and equations used to ensure that the data generated under this quality system meet the established DQOs for each project. Complete definitions of accuracy, precision, completeness, representativeness, comparability, and sensitivity are provided in the R5 QAPP.

The results of QC activities will be compared to the project objectives stated in this QAPP. Only data meeting these specifications will be considered usable for decision making purposes. A team of qualified reviewers will assess these data from a qualitative and a quantitative perspective and the results will be presented and discussed in the appropriate REPA deliverable (as outlined in the approved Work Plan). All project data will be assessed in accordance with the Region 5 DQA Policy and as prescribed in Section 11.3 of this plan.

ELEMENT 15: CORRECTIVE ACTION

Booz Allen's protocols and responsibilities for reporting and implementing corrective actions are defined in the R5 QAPP.

ELEMENT 16: QUALITY ASSURANCE REPORTS TO MANAGEMENT

The type and routine frequency of project level REPA3 quality system reports to management are defined in the R5 QAPP.

APPENDIX A
LABORATORY SOP FOR METHOD 1668

STL KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: Analysis of Polychlorinated Biphenyl (PCB) Isomers by Isotope Dilution HRGC/HRMS

(SUPERSEDES: Revision 1)

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1 Scope and Application

1.1 This procedure is designed to meet analytical program requirements where HRGC/HRMS analysis of polychlorinated biphenyl (PCB) isomers is specified. The procedure is used by STL Knoxville for the detection and quantitative measurement of all 209 PCB isomers in a variety of environmental matrices at part-per-trillion (ppt) to part-per-quadrillion (ppq) concentrations. This procedure is based on EPA method 1668A.

1.2 The compounds listed in Table 1 may be determined by this procedure. The detection limits and quantitation levels in this method are usually dependent on the level of interferences rather than instrumental limitations. The minimum levels (EMLs) in Table 4 are the levels at which the PCBs can be determined with only common laboratory interferences present. The actual limits of detection and quantitation will vary depending on the complexity of the matrix.

1.3 The lower calibration limits of the method are listed in **Table 3** for individual isomers. Analysis of a one-tenth aliquot of the sample permits measurements of concentrations up to 10 times the upper calibration range. Samples containing concentrations of PCB's that are greater than ten times the upper calibration range should be analyzed by protocols designed for such concentration levels.

1.4 The GC/MS portions of this method are for use only by analysts experienced with HRGC/HRMS or under the close supervision of such qualified persons. Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in section 9.1.

1.5 This procedure is based on "performance-based" methods. These reference methods allow modifications to overcome interferences or lower the cost of measurements, if all performance criteria in the methods are met and method equivalency is established. Deviations from the referenced methods have been incorporated into this procedure and are listed in section 17.1. Deviations to this procedure are only allowed as specified in section 11.1.

1.6 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCBs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 5 of this procedure discusses safety procedures.

2 Summary of Method

2.1 Extraction

2.1.1 Aqueous samples (samples containing less than one percent solids): Stable isotopically labeled analogs of the toxic PCBs plus additional labeled PCB's are spiked into a 1-L sample, and the sample is extracted with methylene chloride using separatory funnel techniques.

2.1.2 Solid and semi-solid (but not tissue): The labeled compounds are spiked into a sample containing 10 g (dry weight) of solids. The sample is extracted for 16 hours with an appropriate solvent using a Soxhlet extractor. The extract is concentrated for cleanup. If other analytical protocols are to be performed on the same extract, the extract is split and a separate analysis is performed on each extract fraction.

2.1.3 Multi-phase samples: Samples containing multiple phases are separated and the phases are extracted following the procedures for the appropriate matrix. The extracts may be combined for cleanup and analysis or processed separately. Specific handling of multi-phase samples should be discussed and documented with the project manager prior to extraction of samples.

2.1.4 Fish and other tissue: A 20-g aliquot of sample is homogenized, and a 10-g aliquot is spiked with the labeled compounds. The sample is blended with sodium sulfate, and extracted for 16 hours using methylene chloride:hexane (1:1) in a Soxhlet extractor. A portion of the extract is evaporated to dryness and used to determine the lipid content. The remaining extract is concentrated for cleanup.

2.1.5 Non-aqueous liquids such as oils and organic solvents are diluted or solvent exchanged in hexane.

2.2 After extraction, samples may be cleaned up using back-extraction with sulfuric acid and Florisil column chromatography.

2.3 After cleanup, the extract is concentrated to either 100 µL or 20 µL. Recovery standards are added to each extract, and an aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high-resolution (≥10,000) mass spectrometer. Two exact m/z's are monitored for each analyte.

2.4 An individual PCB congener is identified by comparing the GC retention time and ion-abundance ratio of two exact m/z's with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundance ratio of the two exact m/z's.

2.5 Quantitative analysis is performed using selected ion current profile (SICP) areas, in one of two ways:

2.5.1 For PCBs with labeled analogs (see Table 1), the GC/MS system is calibrated, and the concentration of each compound is determined using the isotope dilution technique.

2.5.2 For PCBs without labeled compounds, the GC/MS system is calibrated and the concentration of each compound is determined using the internal standard technique.

2.6 The quality of the analysis is assured through reproducible calibration and testing of the extraction, cleanup, and GC/MS systems.

3 Definitions

These definitions and purposes are specific to this method but conform to common usage as

much as possible.

Note: Terminology differences existing in some isotope dilution reference methods regarding the functionality of the labeled analogs may lead to confusion. For example, EPA's Office of Solid Waste methods (8280, 8290) use the term "Internal Standards" to describe the labeled analogs which are added to the sample prior to extraction and used to quantitate the native targets. EPA's Office of Water methods (1613B, 1668 Draft) use the term "Labeled Analogs" to describe these same compounds while using the term "Internal Standards" to describe the labeled analogs which are added to the extract just prior to analysis and used to quantitate the recovery of the labeled analogs added before extraction. EPA's Office of Solid Waste methods (8280, 8290) uses the term "Recovery Standards" to describe these later labeled analogs.

The terminology conventions established by the EPA's Office of Solid Waste methods (8280, 8290) are used in the laboratory for all Standard Operating Procedures and internal communications as defined in this section.

3.1.1 Analyte - A PCB tested for by this method. The analytes are listed in Table 1.

3.1.2 Calibration standard (CAL) - A solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration.

3.1.3 Calibration verification standard (VER) - The mid-point calibration standard (CS3) that is used to verify calibration. See Table 6.

3.1.4 Cleanup Standard - Isotopically labeled compound that is added to samples, blanks, quality control samples, and calibration solutions. It is added to the samples after extraction but prior to extract cleanup, and is used to judge the efficiency of the cleanup procedures.

3.1.5 CS0.2, CS1, CS2, CS3, CS4, CS5 - See Calibration standards and Table 6.

3.1.6 Estimated Detection Limit (EDL): The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level.

3.1.7 Estimated Maximum Possible Concentration (EMPC): The calculated concentration of a signal having the same retention time as a PCB congener but which does not meet the other qualitative identification criteria defined in the method.

3.1.8 Estimated Minimum Detection Limit (EMDL) – The lowest concentration at which an analyte can be detected with common laboratory interferences present.

3.1.9 Estimated Minimum Level (EML) – The lowest concentration at which an analyte can be measured reliably with common laboratory interferences present assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures.

3.1.10 Field blank - An aliquot of reagent water or other reference matrix that is placed in a sample container in the laboratory or the field, and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

3.1.11 GC - Gas chromatograph or gas chromatography.

3.1.12 HRGC - High resolution GC.

3.1.13 HRMS - High resolution MS.

3.1.14 ICV: Initial Calibration Verification Standard. A calibration standard from a second source, traceable to a national standard if possible. The ICV is analyzed after the Initial calibration to verify the concentration of the Initial Calibration Standards.

3.1.15 Internal Standards (IS): Isotopically labeled analogs of the target analytes that are added to every sample, blank, quality control spike sample, and calibration solution. They are added to the sample before extraction and are used to calculate the concentration of the target analytes or detection limits.

3.1.16 IPR - Initial precision and recovery; four aliquots of the diluted PAR standard analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed prior to the first time this method is used and any time the method or instrumentation is modified.

3.1.17 K-D - Kuderna-Danish concentrator; a device used to concentrate the analytes in a solvent.

3.1.18 Laboratory blank - See Method blank.

3.1.19 Laboratory control sample (LCS) - See Ongoing precision and recovery standard (OPR).

3.1.20 Laboratory reagent blank - See Method blank.

3.1.21 Method blank - An aliquot of a clean test matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The method blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus.

3.1.22 MS - Mass spectrometer or mass spectrometry.

3.1.23 OPR - Ongoing precision and recovery standard (OPR); a laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

3.1.24 PAR - Precision and recovery standard; secondary standard that is diluted and spiked to form the IPR and OPR.

3.1.25 PFK - Perfluorokerosene; the mixture of compounds used to calibrate the exact m/z scale in the HRMS.

3.1.26 Primary dilution standard - A solution containing the specified analytes that is purchased or prepared from stock solutions and diluted as needed to prepare calibration solutions and other solutions.

3.1.27 Quality control check sample (QCS) - A sample containing all or a subset of the analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

3.1.28 PCB - Polychlorinated biphenyl

3.1.29 Reagent water - Water demonstrated to be free from the analytes of interest and potentially interfering substances at the method minimum level for the analyte.

3.1.30 Recovery Standard (RS): Isotopically labeled compounds which are added to every sample, blank, and quality control spike sample extract prior to analysis. They are used to measure the recovery of the internal standards and the cleanup standards.

3.1.31 Relative Percent Difference (RPD): A measure of the difference between two values normalized to one of the values. It is used to determine the accuracy of the concentration measurements of second source verification standards.

3.1.32 Relative standard deviation (RSD) - The standard deviation times 100 divided by the mean. Also termed "coefficient of variation."

3.1.33 RF - Response factor. See Section 10.2.4.

3.1.34 RRF - Relative response factor. See Section 10.2.4.

3.1.35 RSD - See Relative standard deviation.

3.1.36 SDS - Soxhlet/Dean-Stark extractor; an extraction device applied to the extraction of solid and semi-solid materials.

3.1.37 SICP - Selected ion current profile; the line described by the signal at an exact m/z.

3.1.38 SPE - Solid-phase extraction; an extraction technique in which an analyte is extracted from an aqueous sample by passage over or through a material capable of reversibly adsorbing the analyte. Also termed liquid-solid extraction.

3.1.39 Specificity - The ability to measure an analyte of interest in the presence of interferences and other analytes of interest encountered in a sample.

3.1.40 Stock solution - A solution containing an analyte that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

3.1.41 Surrogate Standards (SS) - Isotopically labeled compounds that are added to XAD samples and calibration solution. They are added to XAD sampling tubes before sampling and are used to measure sampling and recovery efficiency.

3.1.42 VER - See Calibration verification standard.

4 Interferences

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Where possible, reagents are cleaned by extraction or solvent rinse. The non-coplanar PCB congeners 105, 114, 118, 123, 156, 157, 167, and 180 have been shown to be very difficult to completely eliminate from the laboratory at the minimum levels in this method, and baking of glassware in a kiln or furnace at 450 - 500°C may be necessary to remove these and other contaminants.

4.2 Proper cleaning of glassware is extremely important, because glassware may not only contaminate the samples but may also remove the analytes of interest by adsorption on the glass surface. For specific glassware cleaning procedures, see SOP KNOX-QA-0002, current revision, "Glassware Cleaning".

4.3 All materials used in the analysis shall be demonstrated to be free from interferences by running laboratory method blanks (section 9.3) initially and with each sample batch (samples started through the extraction process on a given 12-hour shift, to a maximum of 20 samples).

4.3.1 The method blank consists of reagent water for water samples, sand for solid samples, sodium sulfate for tissue samples, or reagent solvent for waste samples.

4.4 Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the site being sampled. Interfering compounds may be present at concentrations several orders of magnitude higher than the PCBs. The most frequently encountered interferences are chlorinated dioxins and dibenzofurans, methoxy biphenyls, hydroxy-diphenyl ethers, benzylphenyl ethers, polynuclear aromatics, and pesticides. Because very low levels of PCBs are measured by this method, the elimination of interferences is essential. The cleanup steps given in section 11.6 can be used to reduce or eliminate these interferences and thereby permit reliable determination of the PCBs at the levels shown in Table 3.

4.5 Each piece of reusable glassware is numbered to associate that glassware with the processing of a particular sample. This will assist the laboratory in tracking possible sources of contamination for individual samples, identifying glassware associated with

highly contaminated samples that may require extra cleaning, and determining when glassware should be discarded.

4.6 Cleanup of tissue - The natural lipid content of tissue can interfere in the analysis of tissue samples for the PCBs. The lipid contents of different species and portions of tissue can vary widely. Lipids are soluble to varying degrees in various organic solvents and may be present in sufficient quantity to overwhelm the column chromatographic cleanup procedures used for cleanup of sample extracts. Lipids must be removed by the acid cleanup procedure in section 11.6.3, followed by Florisil (section 11.6.4).

5 Safety

5.1 Procedures shall be carried out in a manner that protects the health and safety of all laboratory personnel.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the STL Corporate Safety Manual), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately. VITON gloves may be worn when halogenated solvents are used for extractions or sample preparation. Nitrile gloves may be used when other solvents are handled. [Note: VITON is readily degraded by acetone; all solvents will readily pass through disposable latex rubber gloves.]

5.3 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.3.1 Chemicals that have been classified as **carcinogens**, **potential carcinogens**, or **mutagens include**: benzene, methylene chloride, polychlorinated biphenyls, and toluene. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.)

5.3.2 Chemicals known to be **flammable** are: acetone, benzene, hexane, nonane, tetradecane, and toluene.

5.3.3 The following materials are known to be **corrosive**: sulfuric acid.

5.4 Exposure to chemicals will be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples will be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 The preparation of all standards, reagents, and glassware cleaning procedures that involve solvents will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.6 The effluents of sample splitters for the gas chromatograph and roughing pumps on the mass spectrometer must be vented to the laboratory hood exhaust system or must pass through an activated charcoal filter.

5.7 Training: Workers must complete the employee Corporate Safety Manual safety orientation prior to working in the laboratory.

5.8 Personal Hygiene: Thorough washing of hands and forearms is recommended after each manipulation and before breaks (coffee, lunch, and shifts).

5.9 Confinement: Work areas should be isolated and posted with signs. Glassware and tools should be segregated. Benchtops should be covered with plastic backed absorbent paper.

5.10 Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans.

5.11 Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

5.12 All work must be stopped in the event of a known or potential compromise to the health or safety of laboratory personnel. The situation must be reported immediately to a laboratory supervisor.

6 Equipment and Supplies

Note: All glassware used in extraction and cleanup procedures is solvent rinsed 2 times before use with acetone, methylene chloride and hexane in that order. Pre-extract Soxhlet apparatus with toluene for at least 4 hours. Rerinse the glassware with all 4 solvents once. See SOP KNOX-QA-0002, current revision, "Glassware Cleaning", for details.

6.1 Equipment for sample preparation.

6.1.1 Laboratory fume hood of sufficient size to contain the sample preparation equipment listed below.

6.1.2 Tissue homogenizer - Laboratory blender with glass body and stainless steel blades.

6.1.3 Equipment for determining percent moisture.

6.1.3.1 Oven - Capable of maintaining a temperature of 105 ±5°C.

6.1.3.2 Desiccator.

6.1.4 Balances.

6.1.4.1 Top loading - Capable of weighing 10 mg.

6.2 Extraction apparatus.

6.2.1 Liquid/liquid extraction for water samples.

6.2.1.1 Graduated cylinder, 1-L capacity.

6.2.1.2 Separatory funnels, 250-, 500-, and 2000 mL, with fluoropolymer stopcocks.

6.2.2 Soxhlet/Dean-Stark (SDS) extractor for filters and solid/sludge samples.

6.2.2.1 Soxhlet - 50-mm ID, 200-mL capacity with 500-mL round bottom flask.

6.2.2.2 Soxhlet - 64 mm ID, 500-mL capacity with 1000-mL round bottom flask.

6.2.2.3 Glass condenser, capable of fitting top of Soxhlet or Dean Stark apparatus.

6.2.2.4 Thimble - Whatman high purity glass fiber thimbles

6.2.2.5 Dean Stark moisture trap, with fluoropolymer stopcock, to fit Soxhlet.

6.2.2.6 Heating mantles with temperature controls

6.3 Flasks, Erlenmeyer, 500 mL

6.4 Beakers, 500-mL.

6.5 Spatulas - Stainless steel.

6.6 Fluoropolymer squirt bottles, 500 mL

6.7 Filtration apparatus.

6.7.1 Pyrex glass wool – Solvent rinsed.

6.7.2 Glass funnel – 100 mm with short stem.

6.7.3 Buchner funnel – 15-cm.

6.7.4 Glass-fiber filter paper for Buchner funnel above.

6.7.5 Filtration flasks - 1.5- to 2.0-L, with side arm.

6.8 Cleanup apparatus.

6.8.1 Pipettes.

6.8.1.1 Glass, 1 mL, Class A.

6.8.1.2 Borosilicate glass, disposable, Pasteur, 150-mm long x 5-mm ID.

6.8.1.3 Borosilicate glass, disposable, Pasteur, 230-mm long x 5-mm ID.

6.8.1.4 Pipette Bulbs, rubber, disposable.

6.8.2 Glass chromatographic columns.

6.8.2.1 All disposable columns are solvent rinsed before use. The solvents used are acetone, toluene, methylene chloride and hexane (in this order). Allow to air dry in a hood.

6.8.3 Oven-For baking and storage of absorbents, capable of maintaining a constant temperature (±5°C) in the range of 105-250°C.

6.9 Concentration apparatus.

6.9.1 Kuderna-Danish (K-D) concentrator.

6.9.1.1 Concentrator tube - 10 mL graduated.

6.9.1.2 Evaporation flask - 500 mL, attached to concentrator tube with springs.

6.9.1.3 Snyder column - Three-ball macro.

6.9.1.4 Boiling beads, 6 mm glass

6.9.1.5 Boiling chips. - PFTE - Extracted with methylene chloride.

6.9.1.6 Water bath - Heated, installed in a fume hood.

6.9.2 Nitrogen blowdown apparatus - Rapidvap (Labconco) and/or N-Evap (Organomation Associates, inc., South Berlin, MA), installed in a fume hood.

6.9.3 Sample vials

6.9.3.1 Borosilicate glass, 40 mL disposable with fluoropolymer cap

6.9.3.2 Mini vials, 1.1 mL capacity with a tapered bottom; with Teflon™-faced, rubber septa and screw caps.

6.10 Gas chromatograph - Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specifications in Section 10.

6.10.1 Column #1 - 30 ±5-m long x 0.25±0.02-mm ID; 0.25-µm film SPB-Octyl (Supelco 2-4218, or equivalent).

6.10.2 Column#2 - 60m x 0.32mm ID x 0.25µm film thickness DB-5 or RTX-5 fused silica capillary column (J&W No. 123-5062 or Restek No.10227) or equivalent.

6.11 Mass spectrometer - Electron impact ionization, shall be capable of repetitively selectively monitoring 20 exact m/z's minimum at high resolution (≥10,000) during a period less than 1.0 second, and shall meet all of the performance specifications in Section 10.

6.12 GC/MS interface - The mass spectrometer (MS) shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not

intercept the electron or ion beams.

6.13 Data system - Capable of collecting, recording, and storing MS data.

7 Reagents and Standards

CAUTION: Refer to Material Safety Data Sheets (MSDS) for specific safety information on chemicals and reagents prior to use or as needed.

CAUTION: During preparation of reagents, associates shall wear lab coat, gloves, safety glasses with side shields, face shield (when using concentrated acid) and laboratory approved shoes as a minimum. Reagents shall be prepared in a fume hood.

7.1 Sulfuric acid - Reagent grade (specific gravity 1.84).

7.2 Sodium chloride - Reagent grade, prepare at 5% (w/v) solution in reagent water.

7.3 Sodium sulfate, reagent grade, granular, anhydrous (Baker 3375, or equivalent), baked at 450°C for 4 hour minimum, cooled in a desiccator, and stored in a pre-cleaned glass bottle with fluoropolymer lined screw-cap that prevents moisture from entering. If, after heating, the sodium sulfate develops a noticeable grayish cast (due to the presence of carbon in the crystal matrix), that batch of reagent is not suitable for use and should be discarded. Pre-cleaning of sodium sulfate by extraction with methylene chloride is required if contamination is indicated by reagent tests or method blanks that do not meet quality requirements.

7.4 Purified nitrogen.

7.5 Solvents - Acetone, toluene, n-hexane, 2-propanol, methanol, methylene chloride, ethyl ether and nonane; pesticide quality, from lots that have been approved for use by the Specialty Organics lab.

7.6 Reagent water - Water prepared by passing through carbon bed and ion exchange filters.

7.7 White quartz sand, 60/70 mesh - For Soxhlet/Dean-Stark extraction (Aldrich Chemical, Cat. No. 27-437-9, or equivalent). Bake at 450°C for 4 hour minimum.

7.8 Florisil, Pesticide residue (PR) grade (60/100) mesh; purchased activated at 1250°C (677°F), stored in glass container with fluoropolymer lined top. Fill a clean 1- to 2-L bottle 1/2 to 2/3 full with Florisil and place in an oven at 120-150 °C for a minimum of 6 hours.

7.9 Perfluorokerosene (PFK) high boiling mass spectroscopy grade; bp 210-260°C; d^{20}_4 1.94; n^{20}_D 1.330; Fluka (Catalog No. - 77275).

7.10 Tetrabutylammonium hydrogen sulfate.

7.10.1 Tetrabutylammonium (TBA) sulfite reagent - Prepare the reagent by dissolving 3.39 g of tetrabutylammonium hydrogen sulfate in 100 ml of reagent water. To remove

impurities extract this solution three times with 20 ml portions of hexane. After discarding the last hexane wash slowly add 25 g of sodium sulfite to the solution and shake bottle until the sodium sulfite dissolves. Record the date prepared, initials of the preparer and expiration date on the bottle label. This solution can be stored for 1 month at room temperature in an amber bottle with a Teflon-lined lid.

NOTE: To prepare 50 ml of this reagent, halve the recipe listed above.

7.11 Sodium sulfite.

7.12 Standards and Calibration Solutions: Obtained as prepared solutions from Accustandard (New Haven, CT.), Cambridge Isotope Laboratories (CIL, Andover Massachusetts), and Wellington Laboratories (Guelph, Ontario, Canada). If the chemical purity is 98% or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at room temperature in screw-capped vials with fluoropolymer-lined caps.

7.12.1 Native PCB Calibration Stocks – Twenty-nine primary stock standard solutions are used, with each containing the one of the native isomers listed in Table 5. The stock solutions are purchased at 100 ng/mL in isooctane. Once the ampoule has been sonicated and opened, the solution is transferred to an amber glass vial with fluoropolymer-lined cap and is used as received.

7.12.2 PCB Congener Mix 1 through 5 standard solutions containing all 209 isomers are Certified Reference Standards (Accustandard Product No's. M-1668A-1, M-1668A-2, M-1668A-3, M-1668A-4, M-1668A-5,). Stock solution are purchased at 250-750 µg/mL in isooctane. Once the ampoule has been sonicated and opened, the solution is transferred to an amber glass vial with fluoropolymer-lined cap and is used as received.

7.12.3 Labeled PCB congener solutions used are Certified Reference Standards purchased from Cambridge Isotope Laboratories (CIL, Andover Massachusetts) and Wellington Laboratories (Guelph, Ontario, Canada) (see Table 5). Stock solutions are purchased at 40µg/mL or 50µg/mL in nonane. Once the ampoule has been sonicated and opened, the solution is transferred to an amber glass vial with fluoropolymer-lined cap and is used as received.

7.12.4 Mixed stock standard solutions are prepared by diluting the stock solutions into nonane. The following mixed stock standard solutions are prepared;

7.12.4.1 Native PCB Secondary Stock solution: Prepared by combining the Native PCB Stock solutions referred to in section 7.12.1 and taking to a concentration of 3.0 ug/mL with nonane.

7.12.4.2 209 PCB Primary Stock solution: Prepared by combining the 5 PCB Congener Mixes referred to in section 7.12.2 and diluting to a concentration of 5000-15000 ng/mL in nonane.

7.12.4.3 $^{13}C_{12}$ Labeled Internal Standard stock solution: Prepared by diluting the individual stock solutions of the $^{13}C_{12}$ labeled internal standards listed in section 7.12.3 and Table 5 to a concentration of 1000 ng/mL in nonane.

7.12.4.4 $^{13}C_{12}$ Labeled Recovery Standard stock solution: Prepared by mixing the individual stock solutions of the $^{13}C_{12}$ labeled recovery standards listed in section 7.12.3 and Table 5, resulting in a concentration of 20 ug/mL.

7.12.4.5 $^{13}C_{12}$ Labeled Cleanup Standard Primary Stock solution: Prepared by diluting the individual stock solutions of the $^{13}C_{12}$ labeled cleanup standards listed in section 7.12.3 and Table 5 to a concentration of 5000 ng/mL in nonane.

7.12.4.6 $^{13}C_{12}$ Labeled Surrogate Standard Primary Stock solution: Prepared by diluting the individual stock solutions of the $^{13}C_{12}$ labeled surrogate standards listed in section 7.12.3 and Table 5 to a concentration of 5000 ng/mL in nonane.

7.12.5 Calibration Standard solutions (CS0.2 through CS5) are prepared by dilution of the mixed stock standard solutions prepared in section 7.12.4 in nonane. Table 6 shows the calibration solutions components and final concentrations. This series of solutions is used to establish linearity and relative response factors for those compounds in the initial calibration solutions. These RRFs are used to quantify these nineteen PCB congeners in the calibration verification (VER) and all samples. The CS3 standard is used for calibration verification (VER).) .

7.12.6 209 PCB Congener Calibration Solution – This is a single solution containing all 209 individual PCBs as well as internal standards and recovery standards at the following concentrations:

- mono's, di's, and tri's at 50ng/mL
- tetra's, penta's, hexa's and hepta's at 100ng/mL
- octa's nona's and deca's at 150ng/mL
- internal standards and recovery standards are at the same concentration as the calibration standards (CS1 - CS5)

This solution is always analyzed immediately after the initial calibration to calculate individual RRFs for all individual PCBs (some of which occur as coelutions) for which RRFs are not determined from the initial calibration. This standard also establishes RRT's for all compounds. The RRFs from this single point calibration are used for all congeners not in initial calibration solutions CS0.2 through CS5. These RRFs are used until the calibration verification fails, thereby necessitating repeating the initial calibration. This standard is reanalyzed at least once every three months that samples are analyzed.

Note: The 209 Compound Calibration solution is made up of five mixes that can be obtained from Accustandard. Initially (while setting up for this method) these five mixes must be run separately so the lab can determine the retention times for each of the congeners and which congeners will co-elute. The retention times and elution

orders listed in Table 11 were confirmed by the analysis of individual congener standards procured from Accustandard.

7.12.7 PAR PCB Spiking Solution: Prepared by diluting the PAR PCB Secondary Stock solution prepared in section 7.12.4.1 to the concentration specified in Table 5 with acetone in a volumetric flask. 1.0 mL of this solution is added to each IPR or OPR sample prior to extraction. The concentration of this solution is verified by GC/MS before use.

7.12.8 $^{13}C_{12}$ Labeled internal standard spiking solution: Prepared by diluting the $^{13}C_{12}$ Labeled Internal Standard Stock solution prepared in section 7.12.4.3 to the concentration specified in Table 5 with acetone in a volumetric flask. 1.0 mL of this solution is added to each sample prior to extraction. The concentration of this solution is verified by GC/MS before use.

7.12.9 $^{13}C_{12}$ Labeled Cleanup Standard Spiking solution: Prepared by diluting the $^{13}C_{12}$ Labeled Cleanup Standard Primary Stock solution prepared in section 7.12.4.5 to the concentration specified in Table 5 with hexane in a volumetric flask. 1.0 mL of this solution is added to each sample prior to extraction. The concentration of this solution is verified by GC/MS before use.

7.12.10 $^{13}C_{12}$ Labeled Surrogate Standard Spiking solution: Prepared by diluting the $^{13}C_{12}$ Labeled Surrogate Standard Primary Stock solution prepared in section 7.12.4.6 to the concentration specified in Table 5 with nonane in a volumetric flask. 100 uL of this solution is added to each XAD tube or PUF cartridge prior to sampling. The concentration of this solution is verified by GC/MS before use.

7.12.11 $^{13}C_{12}$ Labeled Recovery Standard Spiking solution: Prepared by diluting the $^{13}C_{12}$ Labeled Recovery Standard Stock solution prepared in section 7.12.4.4 to the concentration specified in Table 5 with nonane in a volumetric flask. 100 uL of this solution is added to each sample extract prior to analysis. The concentration of this solution is verified by GC/MS before use.

7.12.12 QC Check Sample - A QC Check Sample should be obtained from a source independent of the calibration standards. This check sample is a certified standard reference material (SRM) containing the PCBs in known concentrations in a sample matrix similar to the matrix under test. The National Institute of Standards and Technology (NIST) in Gaithersburg, Maryland has an SRM 1944 – New York/New Jersey Waterway Sediment that the NYSDEC recommends for use.

7.12.13 Initial Calibration Verification Standard - A second source standard traceable to a national standard, if available.

8 Sample Collection, Preservation and Storage

8.1 Collect samples in amber glass containers following conventional sampling practices.

Note: Sample preservation, if required, must be performed at the time of collection and is the responsibility of the sample collector in accordance with the clients Quality Assurance Project Plan. The methods referenced in section 16 provide sample collection and preservation guidance which may be used in the absence of a specific Quality Assurance Project Plan.

8.2 Sample Storage

8.2.1 Maintain aqueous samples at 0-4°C from the time of collection until receipt at the laboratory. Store aqueous samples in the dark at 0-4°C.

8.2.2 Maintain solid, semi-solid, oily, and mixed-phase, fish, and adipose tissue samples at <4°C from the time of collection until receipt at the laboratory. Fish and adipose tissue should be shipped with dry ice if at all possible. Store solid, semi-solid, oily, and mixed-phase in the dark at <-10°C, store fish, and adipose tissue samples in the dark at <-10°C.

8.3 Holding Times

8.3.1 If stored according to the conditions specified in 8.2, samples may be stored for up to one year.

8.3.2 Store sample extracts in the dark at room temperature until analyzed. If stored in the dark at room temperature, sample extracts may be stored for up to one year.

9 Quality Control

9.1 Initial precision and recovery (IPR) samples are analyzed to demonstrate the ability to generate acceptable precision and accuracy.

9.1.1 For aqueous samples, extract, concentrate, and analyze four 1-L aliquots of reagent water spiked with labeled internal standards and the precision and recovery standard according to the procedures in section 11. For non-aqueous samples, extract, concentrate, and analyze four aliquots of sand spiked with labeled internal standards and the precision and recovery standard according to the procedures in sections 11. All sample processing steps that are to be used for processing samples, including preparation, extraction, and cleanup shall be included in this test.

9.1.2 Using the results of the set of four analyses, compute the average concentration (X) of the extracts in ng/mL and the relative standard deviation (RSD) of the concentration in ng/mL for each compound.

9.1.3 For each PCB and labeled compound, compare RSD and X with the corresponding limits for initial precision and recovery in Table 10. If RSD and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual RSD exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is

unacceptable for that compound. Correct the problem and repeat the test.

9.2 Internal Standards

9.2.1 Every sample, blank, and QC sample is spiked with internal standards. Internal standard recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits. When properly applied, results from isotope dilution techniques are independent of recovery. The recovery of each internal standard should be within the limits in Table 10. If the recovery is outside these limits the following corrective action should be taken:

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.
- If the recovery of any internal standard is less than 25 percent, calculate the S/N ratio of the internal standard. If the S/N is > 10 and the estimated detection limits (EDL's) are less than the estimated minimum levels (EML's), report the data as is with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the estimated detection limits (EDL's) are greater than the estimated minimum levels (EML's), re-extract and re-analyze the sample. If the ion chromatogram of the PFK lock mass m/z indicates ion suppression in the region where the internal standard elutes, reanalyzing the extract at up to a 1/10 dilution may improve the internal standard recovery. If the poor internal standard recovery is judged to be a result of sample matrix, a reduced portion of the sample may be re-extracted or additional clean-ups may be employed. The decision to reanalyze or flag the data should be made in consultation with the client.

9.2.2 Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.3 Method Blanks

A laboratory method blank must be run along with each analytical batch of 20 or fewer samples. Analyze the blank immediately after analysis of the OPR to demonstrate freedom from contamination. The method blank should not contain any of the compounds of interest at a concentration above the estimated minimum level (EML) shown in Table 4. Corrective action is required when compounds of interest are detected in the method blank above the EML. Re-extraction and reanalysis of all samples associated with a contaminated method blank is required. Investigation of the source of the method blank contamination will be initiated before further samples are extracted.

9.3.1 The method blank must have acceptable internal standard recoveries. If internal standard recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of

contamination. If internal standard recoveries are low and there are reportable analytes in the associated samples re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

9.3.2 Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.4 Instrument Blank

9.4.1 Instruments must be evaluated for contamination during each 12-hour analytical run. This may be accomplished by analysis of a method blank. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of solvent with the internal standards and recovery standards added. It is evaluated in the same way as the method blank.

9.5 Ongoing Precision and Recovery (OPR) Sample

9.5.1 An ongoing precision and recovery (OPR) is prepared and analyzed with every batch of 20 samples. All analytes must be within established control limits specified in Table 10. The OPR is spiked with the compounds listed in Table 5.

9.5.2 If any analyte in the OPR is outside the control limits, corrective action must occur. Corrective action may include re-extraction and reanalysis of the batch.

- If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report.
- If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints the OPR is reported and the failure is documented in the project narrative.

9.6 QC Check Sample - Analyze the QC Check Sample (section 7.12.12) periodically to assure the accuracy of calibration standards and the overall reliability of the analytical process. It is suggested that the QC Check Sample be analyzed at least annually.

10 Calibration and Standardization

10.1 Two types of calibration procedures are required. One type, initial calibration, is required before any samples are analyzed and may be required intermittently throughout sample analyses as dictated by the results of continuing calibration procedures described below. The other type, continuing calibration, consists of analyzing the column performance check solution and a calibration solution (CS3). No samples are to be analyzed until acceptable calibration as described in sections 10.2 and 10.2.7.4 is demonstrated and documented.

10.2 Initial Calibration

Initial calibration is required before any samples are analyzed for PCBs. Initial calibration

is also required if any continuing calibration (section 10.2.7.4) does not meet the required criteria in section 10.2.7.

10.2.1 Prepare multi-level calibration standards containing the compounds and concentrations as specified in Table 6. Calibration standards should be stored at room temperature and preferably in amber vials. Calibration standard solutions have an expiration date of ten (10) years from date of receipt unless otherwise specified by the manufacturer/supplier.

10.2.2 Establish operating parameters for the GC/MS system (suggested operating conditions are displayed in Figure 1 and Figure 2). By using a PFK molecular leak, tune the instrument (see the appropriate instrument manufacturer's operating manual for tuning instructions) to meet the minimum resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK). By using peak matching conditions and the aforementioned PFK reference peak, verify that the exact mass of m/z 380.9760 (PFK) is within 5 ppm of the required value. Document that the resolving power at reduced accelerating voltage of m/z 380.9760 is greater than 10,000 (10 percent valley).

10.2.3 Analyze 2µL of the individual PCB mixtures (section 7.12.2) and set the switch-points for the MID descriptors. The switch-points must be set to insure that the first and last eluting isomer of each homolog group and the labeled internal standards are acquired properly. Determine the retention time of each PCB congener using the elution order information in Table 11.

Note 1: PCB Mixture 5 (M-1668A-5) contains the first and last eluting isomer in each homolog group for the SPB-Octyl column (see Table 7 and Table 11).

Note 2: Laboratory data has indicated that the SPB-Octyl column can exhibit significant differences in performance from column to column. It has also been indicated that the column's performance can change significantly due to oxidation with subsequent changes in congener retention times and elution order. The individual PCB mixtures should be analyzed whenever the column's performance or specific congeners retention times are in doubt.

10.2.4 Analyze 2µL of each of the six calibration standards and calculate the RRF of each compound of interest (target analytes, internal standards, cleanup standards, and surrogate standards) vs. the appropriate reference standard (as specified in Table 2) using the following equation;

$$RRF = \frac{As \times Cis}{Ais \times Cs}$$

where:

As = sum of the areas of the quantitation ions of the compound of interest
Ais = sum of the areas of the quantitation ions of the appropriate reference standard

Cis = concentration of the appropriate reference standard
Cs = concentration of the compound of interest

10.2.5 Calculate the mean relative response factor (mean RRF) and the percent relative standard deviation (RSD) of the relative response factors for each compound of interest in the six calibration standard solutions using the following equations;

$$\overline{RRF}_{n=6} = \frac{1}{n} \times \sum_{i=1}^{n} RF_i$$

$$RSD_{n=6} = \sqrt{\frac{\sum_{i=1}^{n} \left(RF_i - \overline{RF}\right)^2}{n-1}} \times \frac{100}{\overline{RRF}}$$

10.2.6 Analyze 2µL of the 209 PCB Congener standard and calculate the RRF of each congener vs. the appropriate internal standard (as specified in Table 2) using the equation in section 10.2.4. The RRF's from the 209 PCB Congener standard is used for calculating the concentration of congeners that are not in the initial calibration standards. If two or more congeners coelute on the analytical column, calculate a combined RRF for the congeners using the sum of the concentration of the congeners. Use this combined RRF to calculate the concentration of each congener. If a congener which is present in the initial calibration standard coelutes with another congener in the 209 PCB Congener standard, use the mean RRF from the initial calibration to calculate and report the concentration of the ICAL congener and the 209 PCB Congener standard RRF to calculate and report the concentration of the coeluting congener.

10.2.6.1 The absolute retention time of CB 209 must exceed 55 minutes. Otherwise the GC temperature program must be adjusted and the test repeated until the requirement is met.

10.2.6.2 Calculate the relative retention time for all native and labeled isomers, using their retention time references from Table 2. Calculate the relative retention time window using the absolute retention time windows from Table 2.

$$\text{RRT Limit Low} = \frac{RT_A - (RT_{WIN}/2)}{RT_{IS}}$$

$$\text{RRT Limit High} = \frac{RT_A + (RT_{WIN}/2)}{RT_{IS}}$$

Where

RT_A = Retention time of analyte

RT_{IS} = Retention time of RT reference.

RT_{WIN} = Absolute RT window in seconds from Table 2

10.2.7 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met before sample analyses are performed. If acceptable initial calibration is not achieved, identify the root cause, perform corrective action, and repeat the initial calibration. If the root cause can be traced to problems with an individual analysis within the calibration series, repeat the individual analysis and recalculate the percent relative standard deviation. If the calibration is acceptable, document the problem and proceed, otherwise repeat the initial calibration. The mean RF's will be used for all calculations of the nineteen PCB in the standards until the continuing calibration criteria in section 10.3.4 are no longer met. At such time, new mean RF's will be calculated from a new set of injections of the calibration solutions.

10.2.7.1 The percent relative standard deviation (RSD) for the mean relative response factors from the unlabeled native analytes must not exceed ± 20 percent, and those for the labeled internal standards must not exceed ± 35 percent.

10.2.7.2 The S/N for the GC signals present in every SICP must be ≥ 10 for calibration solutions CS1 through CS5. If the S/N ratio is ≤ 2.5 for any target analyte in CS0.2, a five point initial calibration is used for that analyte (section 10.2.5) omitting the RRF for CS0.2.

10.2.7.2.1 An exception to the requirement that S/N ≥ 10 on all SICPs is the secondary ion for dichlorinated biphenyls (m/z 223.9974). High background from PFK fragments at 223.9974 results in noise levels which exceed 10% of the signal height at levels that are reliably quantifiable.

10.2.7.3 The ion abundance ratios for all signals in CS1-CS5 must be within the control limits specified in Table 9.

10.2.7.4 Isomer specificity

When analyzing the 209 PCB congener mix:

10.2.7.4.1 Evaluate and document the percent valley between PCBs 34 and 23. The valley height must be less than 40 percent of the height of the shorter of the two peaks.

10.2.7.4.2 Evaluate and document the percent valley between PCBs 187 and 182. The valley height must be less than 40 percent of the height of the shorter of the two peaks.

10.2.8 Analyze 2µL of the Initial Calibration Verification (ICV) Standard in section 7.12.13. Calculate the concentration of the ICV using the RRF's from the CS3 standard analyzed in section 10.2.4. Calculate the percent difference (%D) between the expected and the calculated ICV concentration using the following formula.

$$\%D = \frac{(C_{Exp} - C_{Calc})}{C_{Exp}} \times 100$$

Where:

C_{Exp} = The expected concentration of the ICV Standard.
C_{Calc} = The calculated concentration of the ICV Standard.

10.2.8.1 The general criteria for percent difference acceptance limits is less than or equal to ±35% for all native and labeled compounds. The warning limits for percent difference is ±35 - 55%.

10.2.8.2 All data associated with compounds with percent differences in the warning limits must be reviewed before acceptance.

10.2.8.3 All data associated with compounds with percent differences outside the warning limits shall be documented as an NCM. Corrective action must be taken and may include the following

- Reanalyze the ICV Standard
- Replace and reanalyze the ICV Standard
- Evaluate the instrument performance
- Evaluate the Initial Calibration Standards

10.3 Continuing Calibration

10.3.1 Continuing calibration is performed at the beginning of a 12-hour period after successful mass resolution check.

10.3.2 Document the mass resolution performance as specified in section 10.2.2 at both the beginning and end of the 12-hour period.

10.3.3 Analyze 2µL of the Daily Calibration Standard Solution (CS3). Calculate the concentration (C) of the compounds of interest (target analytes, internal standards, cleanup standards, and surrogate standards) vs. the appropriate reference standard (as specified in Table 2) using the following equation:

$$C = \frac{As \times Cis}{Ais \times RRF}$$

where:

As = sum of the areas of the quantitation ions of the compound of interest
Ais = sum of the areas of the quantitation ions of the appropriate reference standard
Cis = concentration of the appropriate reference standard
RRF= mean relative response factor from section 10.2.5

10.3.4 Criteria for Acceptable Calibration - The criteria listed below for acceptable

calibration must be met before sample analyses are performed. If the acceptance criteria is met the calibration is deemed to be in control and the RRF's generated from the initial calibration and the 209 PCB Congener standard are used to quantify samples. If acceptable calibration is not achieved, identify the root cause, perform corrective action, and repeat the continuing calibration. If a second consecutive attempt at a continuing calibration fails, two consecutive calibrations must meet the criteria, or an initial calibration must be run before proceeding with client samples.

10.3.4.1 The calculated concentration of each compound of interest (target analytes, internal standards, cleanup standards, and surrogate standards) must be within the limits in Table 10.

10.3.4.2 The S/N for the GC signals present in every SICP (including the ones for the labeled standards) must be ≥ 10.

10.3.4.3 The ion abundance ratios (Table 9) must be within the specified control limits.

10.3.4.4 The relative retention times (RRT) of the 19 PCB congeners in the CS3/VER standard must be within their respective RRT limits calculated in section 10.2.6.2. The absolute retention times (RT) of the internal standards must be within ±15 seconds of the retention times obtained during initial calibration.

10.3.4.5 If PCBs 156 and 157 have been classified as uniquely resolved at the most recent initial calibration, the valley between the two must be less than or equal to 50% the lower of the two peaks. If this cannot be demonstrated, the resolution must be reestablished, or a new initial calibration must be analyzed.

10.3.4.5.1 If the RRT's or RT's are not within the limits above, the GC may not be performing properly. However, routine column maintenance may include removing short amounts of the beginning of the column when active sites or non-volatile compounds in sample extracts cause poor chromatography and loss of specificity. Shortening of the column can cause the RRT's or RT's to fall outside the above limits.

10.3.4.5.2 When the RRT of any compound or the RT of any internal standard is not within the above limits corrective action must be taken. If the GC is not performing properly, correct the problem and repeat the test. If the GC is performing properly but the RRT's or RT's have changed due to routine column maintenance, reanalyze the 209 PCB Congener standard and use the RRT's generated from it and the VER to identify the target analytes. Alternatively, adjust the GC and repeat the test or recalibrate, or replace the GC column and either verify calibration or recalibrate.

10.3.4.6 GC resolution.

When running the 209 PCB congener solution:

10.3.4.6.1 The valley height between PCBs 34 and 23 at m/z 255.9613 shall not exceed 40 percent on the SPB-Octyl column.

10.3.4.6.2 The valley height between PCBs 187 and 182 at m/z 393.8025 shall not exceed 40 percent on the SPB-Octyl column.

10.3.5 Daily calibration must be performed every 12 hours of instrument operation. The 12-hour shift begins with the documentation of the mass resolution followed by the injection of the Continuing Calibration Standard (VER).

11 Procedure

11.1 One time procedural variations are allowed only if deemed necessary in the professional judgement of supervision to accommodate variations in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variations in the procedure, except those specified by project specific instructions, shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist, Project Manager, and QA Manager. If contractually required, the client shall be notified.

Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.2 Samples are extracted by the following procedures depending upon sample matrix. Water samples are prepared by separatory funnel liquid/liquid extraction. Solid samples including soils, sediments, tissues, XAD tubes, PUF cartridges, and solid waste materials are prepared by Soxhlet extraction. Non-aqueous liquid wastes and organic solvents are prepared by waste dilution techniques.

NOTE: Samples should be removed from the refrigerator several hours before extraction and allowed to come to room temperature before measuring the volume or performing the extraction.

11.3 Aqueous Samples (samples containing 1% solids or less.)

11.3.1 Refer to Knoxville SOP, KNOX-QA-0002, current revision, for information on glassware cleaning procedures for extraction glassware.

11.3.2 Place separatory funnels, one for each sample, in the rings attached to the latticework set up in the hood.

11.3.3 Attach the 500 mL KD flask or 500 mL round bottom flask directly beneath the separatory funnel to the 3-prong clamps that are also attached to the latticework in the hood. Connect the concentrator tube to the bottom of the KD flask with a Keck clip and add several boiling stones. If using a round bottom flask, add 6-10 6mm glass beads and boiling stones.

11.3.4 Plug the glass funnel with glass wool and pour in some sodium sulfate (about 1 to 2 inches from the top). Rinse the sodium sulfate with methylene chloride. After the

funnel stops dripping, place the funnel on top of the flask that is fitted with a paper clip to aid in filtering.

11.3.5 Inspect the sample for solids or biphasic sample characteristics. If either condition exists, consult the project manager for further instructions. Mark the level of the sample on the sample bottle in order to measure the volume later and carefully add the sample to the separatory funnel, taking care not to spill any sample. For the method blank and the OPR, use a 1000 mL graduated cylinder to measure 1000 mL of reagent water.

11.3.6 Add 1 mL of the ^{13}C labeled internal standard spiking solution, as specified in section 7.12.8, to the sample. For the IPR or OPR, add 1 mL of the PAR PCB Spiking Solution as specified in section 7.12.7. Record the amount of spike used and the spike standard number in the standards logbook and on the benchsheet.

11.3.7 Add 60 mL of methylene chloride to the sample bottle and shake. Then add the methylene chloride to the separatory funnel.

11.3.8 Extract the sample by shaking the separatory funnel for 2 minutes.

CAUTION: Care should be used while performing this operation. Vent the separatory funnel frequently. Goggles should be worn when performing this procedure.

11.3.9 Allow the water and the methylene chloride to separate for 10 minutes. If it is not separated after 10 minutes, try to break up the emulsion by gently swirling the sample or tilting the separatory funnel on its side.

11.3.10 Drain the methylene chloride from the separatory funnel into the glass funnel that is filled with sodium sulfate, allowing the extract to drip into the KD flask or round bottom flask. Be careful not to allow water to escape the separatory funnel or the sodium sulfate will harden and block the flow of the extract. When an emulsion is present, do not drain the emulsion until the third methylene chloride shake has been completed (see section 11.3.12).

11.3.11 Repeat steps 11.3.7 through 11.3.10 two more times.

11.3.12 After the third methylene chloride portion has filtered through the sodium sulfate, rinse the funnel with approximately 40 mL of methylene chloride.

11.3.13 Remove the separatory funnel from the hood and pour the extracted water into the extracted waters waste carboy.

11.3.14 Fill the empty sample bottle to the marked level with tap water. Pour the tap water into a 1000 mL graduated cylinder. Record the volume of sample used on the benchsheet.

11.3.15 Remove the glass funnel from the top of the KD flask or the round bottom flask, attach a Snyder column to the KD flask or round bottom flask and place in a steam bath or heating mantle. Prewet the Snyder column by adding approximately 1 mL of solvent

through the top. Adjust the water temperature or heating mantle as required to achieve the proper rate of distillation. At the proper rate, the balls of the column will actively chatter but the chambers will not flood.

11.3.16 Once the sample is concentrated down to 10 mL, add 50 mL of hexane and concentrate to approximately 10 mL again. Do not allow the sample to go to dryness at any time!

11.3.17 If a KD flask is used, remove the Snyder column, then rinse the KD flask with 2 mL of hexane; that is allowed to drain into the concentrator tube. The concentrator tube is then taken off the KD flask and the ground glass joint of the KD flask is rinsed with a small amount of hexane into the concentrator tube. The sample is then either transferred to a 40 mL vial for acid wash or the concentrator tube is placed on the nitrogen blowdown apparatus and the volume is reduced to 2 mL in preparation for running the sample through Florisil column clean-up. Do not allow the sample to go to dryness at any time!

11.3.18 If a round bottom flask is used, remove the Snyder column, then transfer the extract into a 40 ml vial and then rinse three times with 3 ml (each time) of hexane. The sample is then either ready for acid wash or the 40mL vial is placed on the nitrogen blowdown apparatus and the volume is reduced to 2 mL in preparation for running the sample through florisil column clean-up. Adjust the final volume of the extract with hexane to 15 mL for acid cleanup or 2 mL for column cleanup. Do not allow the sample to go to dryness at any time!

11.3.19 Proceed to section 11.6.

11.4 Solid Sample Extraction (samples containing more than 1% solids.)

11.4.1 Sample Pretreatment

11.4.1.1 Tissue Samples

11.4.1.1.1 If the sample matrix is tissue and has not been homogenized prior to sample receipt, the entire sample is blended to provide a homogeneous sample.

11.4.1.1.2 Cut tissue into pieces of a uniform size (approximately 1 inch square). Homogenize the tissue sample in a laboratory blender.

11.4.1.1.3 Weigh out 10 grams of the homogenized tissue sample. Add the 10 g sample along with 20 g of sodium sulfate to a laboratory blender. Blend the tissue/sodium sulfate mixture, while adding dry ice as necessary, to achieve a powder like consistency.

11.4.1.1.4 Record the sample and weight on the sample prep sheet.

11.4.2 Soxhlet Extraction

11.4.2.1 Prepare and label the required number of Soxhlet systems.

11.4.2.1.1 The Soxhlet is prepared by cleaning and rinsing per section 6, adding an extraction thimble and glass wool plug to the Soxhlet body, charging the boiling flask with solvent, assembling the components, and precleaning by reflux for 4 hours before use.

11.4.2.2 Transfer a well-mixed 10 g aliquot of the solid sample, or the pretreated sample into a glass microfiber extraction thimble (+/- 0.05 grams). Record the sample and weight on the sample prep sheet. If the entire sample is to be analyzed (XAD, filters, etc.), transfer the entire sample to the Soxhlet extractor. If an extraction thimble is not being used, sandwich the sample between glass wool plugs in the extractor. Small portions of acetone may be used to aid in the transfer of XAD. If necessary, weigh the XAD sampling tube both before and after the XAD is removed and record the weights.

11.4.2.3 Sand, baked at 450° C, is used for the blank and OPR. Transfer 10g of sand into an extraction thimble. Record the sample weight on the sample prep sheet.

11.4.2.3.1 If the matrix is tissue samples, sodium sulfate is used for the blank and OPR. Transfer 20 grams of the sodium sulfate and several small chips of dry ice into an extraction thimble. Record the sample weight on the sample prep sheet.

11.4.2.4 Spike each sample with 1 mL of the internal standard solution (see section 7.12.8) and add a small amount of glass wool to the top of the extraction thimble.

11.4.2.4.1 Spike the OPR with 1 mL of the native spiking solutions (see section 7.12.7) prior to adding the glass wool.

11.4.2.5 Pour approximately 350 mL of the extraction solvent into a 500 mL round bottom flask. Place the flask in the heating mantle. Add about 10-15 boiling beads and several Teflon™ boiling chips.

Note: Hexane/Acetone is the preferred solvent to be used for extraction but in certain cases (i.e. XAD extraction) MeCl2/Acetone may be a better choice.

11.4.2.6 Place the extraction thimble in the glass Soxhlet extractor.

11.4.2.7 Assemble the Soxhlet system and secure to the lab supports.

11.4.2.8 Adjust the temperature of the heating mantle to bring the solvent in the round bottom flask to a rolling boil. There should be a steady drip from the condensers so that the solvent should completely cycle at least 5 times an hour.

11.4.2.9 Soxhlet extract the sample in the above manner for 16 hours.

11.4.2.10 Turn off the heating mantle and allow the Soxhlet apparatus to cool.

11.4.2.11 Remove the condensers and allow the Soxhlet extractor chamber to empty, then remove the Soxhlet extractor from the 500 mL round bottom flask. Add a few Teflon™ boiling chips to allow smooth boiling.

11.4.2.12 Insert a three-ball macro Snyder column into the top of the 500 mL round flask. Prewet the Snyder column by adding approximately 1 mL of solvent through the top.

11.4.2.13 Place the 500 mL flask back into the heating mantle and reduce the extract volume to approximately 5 mL. Alternatively, transfer the extract to the Rapidvap concentrator tube rinsing the 500 mL flask 3 times with small amounts of MeCl2/Acetone or Hexane/Acetone. Add the rinsings to the concentrator tube and evaporate the extract to 1 mL using the Rapidvap vortex concentrator. Do not allow the sample to go to dryness at any time!

11.4.2.14 Transfer the extract into a 40 mL vial, rinsing the 500 mL flask or concentrator tube 3 times with 3 mL of MeCl2/Acetone or Hexane/Acetone. Add the rinsings to the 40 mL vial.

11.4.2.15 Place the 40 mL vials into the N-EVAP concentration device and reduce the volume to approximately 0.5 mL. Do not allow the sample to go to dryness at any time. Add 5 mL of hexane and swirl the vial. Reduce the volume of hexane to approximately 0.5 mL again to complete the solvent exchange. Adjust the final volume of the extract with hexane to 15 mL for acid cleanup or 2 mL for column cleanup. If the sample exhibits poor solubility in hexane, add approximately 1 mL of benzene with a pipette to the vial to aid in dissolving the sample. Proceed to section 11.6.

11.5 Waste Sample Extraction

11.5.1 Organic wastes, oil, solids that will dissolve in solvent, and non-aqueous sludge samples may be prepared by the waste dilution technique.

11.5.2 Add an appropriate amount of sample (e.g. 1.0g) to a 40 mL VOA vial. Spike the sample with 1 mL of the internal standard spiking solution (see section 7.12.8). Record the spike solution number and the volume spiked. Add hexane to bring the volume to 15 mL. If the sample exhibits poor solubility in hexane, add approximately 1 mL of benzene with a pipette to the vial to aid in dissolving the sample. Proceed to section 11.6.

11.5.3 Record the weights and volumes used on the laboratory bench sheets.

11.6 Extract Cleanup

11.6.1 If the sample is to be analyzed for PCB's only, use the entire extract for the cleanup procedures. If additional analyses (example: Dioxins, Pesticides, PAH's, or Semi-volatiles) are to be performed on the extract, split the extract in equal portions for each

analysis. Label each split portion with the sample ID and the analysis. Proceed with cleanup on the portion labeled for PCB analysis.

11.6.2 Spike each sample extract with 1 mL of the cleanup standard solution (see section 7.12.9).

11.6.3 Acid Cleanup

11.6.3.1 The acid cleanup is employed when sample extracts are colored and/or oily in appearance.

11.6.3.2 Slowly add 15 mL of concentrated sulfuric acid to the 15 mL extract in the 40 mL vial and shake for 2 minutes. If an emulsion forms, discontinue shaking. Vent the vial frequently while shaking. Let the vial stand for a minimum of 10 minutes and remove the aqueous layer with a glass pipette. Repeat the acid washing until no color is visible in the acid layer (perform a maximum of four acid washings).

11.6.3.3 Add 15 mL 5% (w/v) aqueous sodium chloride to the vial and gently shake for 2 minutes. Vent the vial frequently while shaking. Let the vial stand for 10 minutes and remove the aqueous layer with a glass pipet. Dry the hexane extract by adding 1 to 2 grams of sodium sulfate and swirling the vial.

11.6.3.4 Reduce the extract volume to approximately 2 ml.

11.6.3.5 Proceed to florisil cleanup.

11.6.4 Florisil Column Cleanup

11.6.4.1 Place a small ball of glass wool in the bottom of a glass chromatography column.

11.6.4.2 Attach the column to the lab support in the hood.

11.6.4.3 Pack the florisil column with the following layers. Add the column packing while tapping the column to settle the contents to prevent channeling. The order of the layers is from bottom to top.

11.6.4.3.1 Layer 1 - 8 cm (15 g) of florisil

11.6.4.3.2 Layer 2 - 2 cm (2 g) of sodium sulfate.

11.6.4.4 Place a 500 mL KD or 500 mL round bottom flask under each column to catch the solvents as they filter through the column.

11.6.4.5 Pour 200 mL of 6% diethyl ether in hexane (v/v) into a graduate cylinder and save for later use in the procedure (one graduate cylinder for each column).

11.6.4.6 Wet the column with hexane to remove any air bubbles and discard this hexane into the solvent waste. Take care not to let the column drip dry at any time during this procedure.

11.6.4.7 Just before the level of hexane reaches the top of the sodium sulfate layer, transfer the sample extract into the top of the column. Rinse the vial 3 times with 2 mL portions of hexane and add these rinsings to the column.

11.6.4.8 Just before the sample volume reaches the top of the sodium sulfate, pour the 200 mL of 6% diethyl ether in hexane (v/v) into the top of the column and allow this to drip through the column and into the 500 mL KD flask.

11.6.4.9 Insert a three-ball macro Snyder column into the top of the 500 mL flask. Prewet the Snyder column by adding approximately 1 mL of solvent through the top.

11.6.4.10 Place the 500 mL flask into the steam bath or heating mantle and reduce the extract volume to approximately 5 mL.

11.6.4.11 If a KD flask is used, remove the Snyder column, then rinse the KD flask with 2 mL of hexane that is allowed to drain into the concentrator tube. The concentrator tube is then taken off the KD flask and the ground glass joint of the KD flask is also rinsed with a small amount of hexane into the concentrator tube.

11.6.4.12 If a round bottom flask is used, remove the Snyder column, then transfer the extract into a 40 ml vial and then rinse three times with 3 ml (each time) of hexane. Place the concentrator tube or 40 mL vial containing the extract in the N-EVAP concentration apparatus and reduce the solvent volume to approximately 0.3 ml.

11.6.4.13 Transfer the concentrated extract into a 1.1 mL tapered mini-vial, rinsing 2 times with small amounts of hexane. Label the mini vial with the sample ID.

11.6.4.14 For all samples, add 100 µL of the recovery standard solution (see section 7.12.11) to the mini-vial before transferring the extract into the minivial. Then reduce the extract volume back down to 100 µL. Take the mini-vial to the GC/MS lab for analysis. If the extract has been split for other analyses, adjust the final volumes and recovery standard amounts by the split factor to achieve a comparable analysis sensitivity (example: Extract split in half for PCB and Dioxin analysis, use 50 µL of recovery standard solution and concentrate to a final volume of 50 µL).

11.6.5 Sulfur clean-up by Tetrabutylammonium (TBA)

11.6.5.1 Bring the sample extract to between 5 ml and 10 ml in a 40 ml vial. Caution: Do not let the extract volume drop below 1 ml, as loss of analytes may occur.

11.6.5.2 Add 1.0 ml of TBA sulfite reagent and 2.0 ml of 2-propanol to the vial containing the extract. Shake the vial vigorously for 1 minute.

11.6.5.3 If the extract is colorless or the initial color is unchanged and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more sodium sulfite in approximately 0.10 g portions until a solid residue remains after repeated shaking.

11.6.5.4 Add 5ml of reagent water and shake the vial for 1 minute. Allow the layers to separate (at least 5 minutes). Filter the hexane layer (the top layer) through a small funnel filled with sodium sulfate that has been pre-wetted with hexane and into a clean 40 ml vial.

11.6.5.5 Add 2 ml of fresh hexane to the clean-up vial. Shake for 30 seconds and allow the layers to separate again. Filter the hexane portion through the sodium sulfate funnel and into the clean 40ml vial.

11.6.5.6 Repeat step 11.6.5.5 once.

11.6.5.7 Rinse the sodium sulfate funnel with 2ml of hexane.

11.6.5.8 Proceed to section 11.6.4.13 for final concentration and transfer to a mini-vial

11.7 Sample Analysis

11.7.1 Analyze the sample extracts under the same instrument operating conditions used to perform the instrument calibrations. Inject 2 µL into the GC/MS and acquire data beginning at 8 minutes and ending after decachlorobiphenyl has eluted from the column.

11.7.2 Record analysis information in the instrument logbook. The following information is required:

Date of analysis
Time of analysis
Instrument data system filename
Analyst
Lab sample identification

Additional information may be recorded in the logbook if necessary.

11.7.3 Generate integrated ion chromatograms for the masses listed in Table 8 that encompass the expected retention windows of the PCB homologous series.

12 Data Analysis and Calculations

12.1 Qualitative identification criteria for PCBs.

For a gas chromatographic peak to be identified as a PCB, it must meet all of the following criteria:

12.1.1 The signals for the two exact m/z's in Table 8 must be present and must maximize within ±2 seconds.

12.1.2 The signal to noise ratio (S/N) for each GC peak at each exact m/z must be greater than or equal to (≥) 2.5. (This requirement does not apply to the secondary ion for dichlorinated biphenyls [m/z 223.9974]. High background from PFK fragments at

223.9974 results in noise levels which exceed 10% of the signal height at levels that are reliably quantifiable.)

12.1.3 The ratio of the integrated areas of the two exact m/z's specified in Table 8 must be within the limits in Table 9. Alternately, the ratios may be within ±15% of the ratio in the midpoint (CS3) calibration or calibration verification (VER), whichever is most recent.

12.1.4 The relative retention time of the peak for a CB must be within the RRT QC limits calculated in section 10.2.6.2.

Note: For native CBs determined by internal standard quantitation, a given CB congener may fall within more than one RT window and be misidentified unless the RRT windows are made very narrow, as in Table 2. Therefore, consistency of the RT and RRT with other congeners and the labeled compounds may be required for rigorous congener identification. Retention time regression analysis may be employed for this purpose.

12.1.5 If identification is ambiguous, (i.e. some, but not all of the identification criteria are met for a congener) an experienced analyst must determine the presence or absence of the congener.

12.2 Quantitation for PCB's.

12.2.1 Calculate the Internal Standard Recoveries (Ris) relative to the Recovery Standard according to the following equation:

$$Ris = \frac{Ais \times Qrs}{Ars \times RRFis \times Qis} \times 100\%$$

where:

Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Ars = sum of the areas of the quantitation ions of the recovery standard
Qrs = ng of recovery standard added to extract
Qis = ng of internal standard added to sample
RRFis = mean relative response factor of internal standard obtained during initial calibration

Note: In some situations, such as source testing, the extract is split for multiple analyses. In this case, Qrs must be correctly calculated to account for the splitting of extracts before the recovery standard was added.

$$Qrs = Qrss \times Split$$

where:

Qrs = ng of recovery standard added to extract
Qrss = ng of recovery standard added to the split portion of the extract

Split = split ratio of the extract

12.2.2 Calculate the concentration of individual PCBs according to the following equation:

$$\text{Concentration} = \frac{\text{As} \times \text{Qis}}{\text{Ais} \times \text{RRF} \times \text{W} \times \text{S}}$$

where:

As = sum of the areas of the quantitation ions of the compound of interest
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Qis = ng of internal standard added to sample
RRF = mean relative response factor of compound obtained during initial calibration
W = amount of sample extracted (grams or liters)
S = decimal expression of solids (optional, if results are requested to be reported on dry weight basis)

12.2.3 If reporting results for Total Homolog Groups, calculate the total concentration of all isomers within each homolog group by summing the concentrations of the individual PCB isomers within that homolog group.

12.2.4 If no peaks are present in the region of the ion chromatogram where the compounds of interest are expected to elute, calculate the estimated detection limit (EDL) for that compound according to the following equation:

$$\text{EDL} = \frac{\text{N} \times 2.5 \times \text{Qis}}{\text{His} \times \text{RRF} \times \text{W} \times \text{S}}$$

where:

N = sum of peak to peak noise of quantitation ion signals in the region of the ion chromatogram where the compound of interest is expected to elute
His = sum of peak heights of quantitation ions for appropriate internal standard
Qis = ng of internal standard added to sample
RRF = mean relative response factor of compound obtained during initial calibration
W = amount of sample extracted (grams or liters)
S = decimal expression of solids (optional, if results are requested to be reported on dry weight basis. Note: do not use if results are to be reported by QuantIMS since it performs all necessary moisture corrections.)

12.2.5 If peaks are present in the region of the ion chromatogram which do not meet the qualitative criteria listed in section 12.1, calculate an Estimated Maximum Possible Concentration (EMPC). Use the equation in section 12.2.2, except that As should represent the sum of the area under the one peak and of the other peak area calculated using the theoretical chlorine isotope ratio. The peak selected to calculate the

theoretical area should be the one which gives the lower of the two possible results (i.e. the EMPC will always be lower than the result calculated from the uncorrected areas).

12.2.6 If the concentration in the final extract of any PCB isomer exceeds the upper method calibration limits, a dilution of the extract or a re-extraction of a smaller portion of the sample must be performed. Dilutions of up to 1/10 may be performed on the extract. If compound concentrations exceeding the calibration range cannot be brought within the calibration range by a 1/10 dilution, extraction of a smaller aliquot of sample may be performed or the sample may be analyzed by a more appropriate analytical technique such as HRGC/LRMS. Consultation with the client should occur before any re-extraction is performed. The lab may report the measured concentration and indicate that the value exceeds the calibration limit by flagging the results with "E". Consultation with the client should occur before compounds are reported which exceed the calibration range.

12.3 The estimated minimum level (EML) is defined as the lowest concentration at which an analyte can be measured reliably with common laboratory interferences present assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures. The EML's for different matrices and extract volumes are listed in Table 4. Deviations from the extraction amounts or final volumes listed will result in corresponding changes in the actual sample ML.

12.4 Flag all compound results in the sample which are below the estimated minimum level with a "J" qualifier.

12.5 Flag all compound results in the sample which were detected in the method blank with a "B" qualifier.

12.6 Flag all compound results in the sample which are above the upper calibration limit with an "E" qualifier.

12.7 Flag all compound results in the sample which are "Estimated Maximum Possible Concentrations" with a "Q" qualifier.

12.8 Flag compound results in the sample that may contain co-eluting compounds with a "C" qualifier.

12.8.1 Flag congeners known to coelute with a higher numbered congener with a "C" qualifier.

12.8.2 Flag congeners that coelute with a lower numbered congener with a "Cx" qualifier where x is the CAS PCB number of the lowest numbered congener in the coeluting group.

12.9 Flag compound results in the sample that may be affected by ion suppression with a "S" qualifier.

12.10 Data review

12.10.1 The analyst who performs the initial data calculations must initial and date the front chromatogram of the raw data package to document that they have performed the qualitative and quantitative analysis on the sample data.

12.10.2 A second analyst must verify all qualitative peak identifications. If discrepancies are found, the data must be returned to the analyst who performed the initial peak identification for resolution.

12.10.3 A second analyst must check all hand calculation and data entry into calculation programs, databases, or spreadsheets at a frequency of 100 percent. If discrepancies are found, the data must be returned to the analyst who performed the initial calculation for resolution.

12.10.4 The reviewing analyst must initial and date the front chromatogram of the raw data package to document that they have performed the second level review on the sample data.

12.10.5 All items listed on the data review checklist must be checked by both the analyst who performed the initial qualitative and quantitative analysis and the analyst who performed the second level review. An example data review checklist is shown in Figure 3.

13 Method Performance

13.1 Method Detection Limit

Each laboratory must generate a valid method detection limit for representative analytes of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005.

13.2 Training Qualification

The group/team leader has the responsibility to ensure that an associate who has been properly trained in its use and has the required experience performs this procedure.

14 Pollution Prevention

14.1 All attempts will be made to minimize the use of solvents and standard materials.

15 Waste Management

15.1 Waste generated in this procedure must be segregated and disposed according to the facility hazardous waste procedures.

16 References

16.1 STL Quality Management Plan. (current revision)

16.2 USEPA SW-846 "Test Methods for Evaluating Solid Waste" Third Edition.

16.3 Method 1613: Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS [Revision B], EPA#: 821/B-94-005a YEAR: 1994

16.4 Method 1668: Toxic Polychlorinated Biphenyls by Isotope Dilution High Resolution Gas Chromatography/High Resolution Mass Spectrometry [Draft], EPA#: 821/R-97-001 YEAR: 1997.

16.5 Ballschmiter, K. and M. Zell, "Analysis of Polychlorinated Biphenyls (PCB) by Glass Capillary Gas Chromatography", *Fresenius Z. Anal. Chem.*, 302:20-31 (1980).

16.6 Schulte, E. and R. Malisch, "Berechnung der Wahren PCB-Gehalte in Umweltproben I. Ermittlung der Zusammensetzung Zweier Technischer PCB-Gemische," *Fresenius Z. Anal. Chem.*, 314:545-551 (1983).

16.7 Guitart, R., P. Puig and J. Gómez-Catalán, "Requirement for a Standardized Nomenclature Criterion for PCBs: Computer-Assisted Assignment of Correct Congener Denomination and Numbering," *Chemosphere*, 27(8):1451-1459 (1993).

16.8 Rigaudy, J. and Klesney, S.P., Nomenclature of Organic Chemistry, Pergamon, 1979.

16.9 Pretsch, Clerc, Seibl, Simon, Tables of Spectral Data for Structure Determination of Organic Compounds, Second Edition, Springer-Verlag, 1989.

16.10 CRC Handbook of Chemistry and Physics, 71st edition, CRC Press, 1990-1991.

17 Miscellaneous

17.1 Deviations from EPA Method 1668, Revision A.

17.1.1 The labeled congeners included in the method solely as LOC markers (i.e., 1, 4, 19, 54, 104, 155, 188, 202 and 208) are not used in this procedure. The unlabeled analogs are used in the continuing calibration standard, and are present in OPRs. This provides a demonstration that all congeners in each LOC are acquired for. The method includes a note in section 10.5.3 (of the method), which reads: "All labeled congeners at each LOC are used to reduce the effect of an interference if a single congener is used as a reference. Other quantitation references and procedures may be used provided that the results produced are as accurate as results produced by the quantitation references and procedures described in this section."

17.1.2 A solvent mixture of acetone: hexane (1:1 volume) is used instead of toluene for extractions of solids and samples containing particles.

17.1.3 The method authors had observed that when their columns were degraded, PCBs 156

and 157 became resolved. The method indicates that the compounds must coelute within 2 seconds. Using constant flow conditions, this laboratory has resolved PCB 156 from PCB 157 on columns that are not degraded. This procedure does not require the coelution of the two isomers, but requires that the retention times may not change significantly in relative retention times, in accordance with section 10.3.4.4.

17.1.4 The calibration verification procedures in the method call for updating the retention times, relative retention times and response factors for non-Toxic compounds during daily calibration and use the retention times, relative retention times and response factors from the initial calibration for Toxic and LOC compounds. This laboratory uses the retention times, relative retention times and response factors from the initial calibration for all 209 compounds. The practice of updating the relative retention times of only a subset of compounds causes significant error in the linear regression prediction formulas used by targeting software to identify the compounds.

17.1.5 The EMLs listed in Table 4 differ from those listed in the reference method. The EMLs are set above the worst-case contaminant concentrations at each level of chlorination. The EMLs provided are based on historical blank data and calibration data obtained while performing EPA 1668mod. The survey period was approximately 2 years. During this period, blank contamination exceeded the EMLs twice. These levels are also consistent with ML's maintained by the laboratory while performing in house HRMS PCB analysis over the 10 years preceding the adoption Method 1668.

17.2 Summary of modifications to SOP from previous revisions.

17.2.1 Revision 0 of method.

17.2.2 Revision 1 of method

17.2.2.1 Replaced Proprietary Information Statement and removed references to Quanterra where appropriate.

17.2.2.2 Updated GC Conditions in Figure 1.

17.2.2.3 Corrected PCB Isomer 202L name in Table 5 and Table 6.

17.2.2.4 Changed Quantitation Reference for other Penta's, Hexa's and Hepta's in Table 2.

17.2.2.5 Added 2-propanol to the list of solvents

17.2.2.6 Added tetrabuytlammonium hydrogen sulfate and the preparation of TBA sulfite to the reagent section

17.2.2.7 Added a note to Section 7.10.1 for preparation of reduced volume of TBA Sulfite.

17.2.2.8 Deleted note from Section 11.4.2.5.

17.2.2.9 Replaced "toluene" with references to other solvents in Sections 11.4.2.8, 11.4.2.13, and 11.4.2.14.

17.2.2.10 Deleted references to SDS collectors in Sections 11.4.2.9 and 11.4.2.11.

17.2.2.11 Added the procedure for sulfur removal by TBA sulfite in Section 11.6.5.

17.2.2.12 Added PCB 81 as an analyte, 13C PCB 81 as an internal standard, and 13C PCB 32 as a cleanup standard to Table 1, Table 2, Table 5, Table 6 and Table 10.

17.2.2.13 Added PCBs 1, 4, 19, 37, 54, 104, 155, 188, 202 and 208 to Table 5 and Table 6 as level of chlorination markers.

17.2.2.14 Set concentrations of Native PCBs in Table 6 equal to the levels recommended in EPA 1668A.

17.2.2.15 Amended Table 5 to reflect the catalog numbers for Accustandard individual standard solutions.

17.2.2.16 Amended Table 3 to reflect estimated minimum levels based on the calibration range recommended in EPA 1668A.

17.2.2.17 Amended Table 10 to reflect EPA 1668A spike levels, and acceptance criteria.

17.2.2.18 The requirement for demonstrating proper ion abundance ratios is changed, and is now only required for CS1, as specified by the method. Section 10.3.4.3.

17.2.2.19 Changed formulas to incorporate split ratios in Sections 12.2.1 and 12.2.4.

17.2.2.20 Added columns to Table 2 to show retention time, example retention time windows, relative retention times, and retention time limits.

17.2.2.21 Added sections 12.8.1 and 12.8.2 describing the use of Cx qualifiers.

17.2.2.22 Amended Table 7 to refer PCBs 23,34,182 and 187 as GC resolution test compounds.

17.2.2.23 Amended section 7.12.4 through 7.12.11 to reflect updated stock solution concentrations.

17.2.3 Revision 2 of Method

17.2.3.1 Removed Section 7.12.4.6, Section 7.12.4.8 and Section 7.12.4.9, which specified the preparation of unnecessary intermediate stock solutions.

17.2.3.2 Corrected 7.12.7 to refer to 7.12.4.1 rather than 7.12.4.9. Changed reference to Table 5 to refer to Table 4.

17.2.3.3 Changed Table 4 to reflect higher concentrations of intermediate stocks.

17.2.3.4 Changed concentration listed in 7.12.4.5 from 1000 ng/mL to 5000 ng/mL.

17.2.3.5 Removed 7.12.4.6 and 7.12.4.8.

17.2.3.6 Removed PCBs 28 and 194 from Table 10. Added PCBs 37 and 205 to Table 10.

17.2.3.7 Removed PCB 37 from Section 17.1.1.

17.2.3.8 Added m/z 268.0016 and m/z 269.9986 to MID group 1 in Table 8, to monitor for the cleanup standard ^{13}C-PCB-32. Updated Figure 2.

17.2.3.9 Changed action level in section 9.2.1 to 25%.

17.2.3.10 Clarified ion ratio requirement in section 10.2.7.3.

17.2.3.11 Made minor language changes to sections 2.1.1, 2.3, 5.7, 7.5, 7.12.6, 11.3.15, 11.3.16, 11.3.17, 11.3.18, 11.4.2.5, 11.4.2.13, 11.4.2.15.

17.2.3.12 Added the following requirement to Section 10.3. "If a second consecutive attempt at a continuing calibration fails, two consecutive calibrations must meet the criteria, or an initial calibration must be run before proceeding with client samples."

17.2.3.13 Changed "each laboratory" to "the laboratory" and changed "each analyte" to "representative analytes" in section 13.1.

17.2.3.14 Changed references to "minimum level" to "estimated minimum level" in sections 3, 9.2.1, 12.3, and 12.4.

17.2.3.15 Added requirement that preparer's initials and expiration date be added to labels on TBA sulfite reagents in section 7.10.1.

17.2.3.16 Removed comments that acceptance criteria are considered preliminary from sections 9.1.3, 9.5.1, and Table 9.

17.2.3.17 Revised the equation in section 10.2.5.

17.2.3.18 Converted units in Table 3 to nanograms and millileters.

17.2.3.19 Inserted Table 4, and renumbered Tables 4-9 to 5-10 respectively.

17.2.3.20 Provided for an exception to the s/n requirements for the secondary ion for dichlorinated biphenyls in sections 10.2.7.2.1 and 12.1.2

17.2.3.21 Added sections 3.1.14, 3.1.31, 7.12.13, and 10.2.8.

17.3 List of tables and figures referenced in the body of the SOP.

17.3.1 Table 1 - Polychlorinated Biphenyls Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography (HRGC)/High Resolution Mass Spectrometry (HRMS)

17.3.2 Table 2 - Quantitation and Retention Time References Shown With Example Relative Retention Time Windows and Retention Time Limits

17.3.3 Table 3– Estimated Minimum Levels Based on Various Final Extract Volumes

17.3.4 Table 5-Concentration of Stock & Spiking Solutions Containing PCBs & Labeled Compounds

17.3.5 Table 6 - Concentration of PCBs in Calibration and Calibration Verification Solutions

17.3.6 Table 7 - Window Defining Mixture and SPB-Octyl Resolution Test Compounds

17.3.7 Table 8 - Ions Monitored for HRGC/HRMS Analysis of PCBs

17.3.8 Table 9 - Theoretical Ion Abundance Ratios and Their Control Limits for PCBs.

17.3.9 Table 10-Acceptance Criteria for Performance Tests

17.3.10 Table 11- Retention Times of Isomers on SPB-Octyl Column for PCB Standard Mixes

17.3.11 Figure 1 - Recommended GC Operating Conditions

17.3.12 Figure 2 - Recommended MID Descriptors

17.3.13 Figure 3- Example Data Review Checklist

17.3.14 Figure 4- Analysis of PCB's by HRGC/LRMS (Flowchart)

17.3.15 History of Revisions

REV NO.	DATE	PAGES AFFECTED	REASON FOR REVISION
0	09/28/99	All	Initial Revision of Method
1	10/12/01	See section 17.2.2	Updated based on EPA1668A
2	01/17/02	See section 17.2.3	Updated based on EPA1668A

Table 1

Polychlorinated Biphenyls Determined by HRGC/HRMS

BZ/IUPAC Number[1]	PCB Chemical Structure Name[2]	CAS Registry[3] Number	Labeled Analog	CAS Registry[3]	Usage
1	2-monochlorobiphenyl	2051-60-7			
2	3-monochlorobiphenyl	2051-61-8			
3	4-monochlorobiphenyl	2051-62-9	$^{13}C_6$-4-monochlorobiphenyl $^{13}C_{12}$-4-monochlorobiphenyl		Recovery Std Internal Std
4	2,2'-dichlorobiphenyl	13029-08-8			
5	2,3-dichlorobiphenyl	16605-91-7			
6	2,3'-dichlorobiphenyl	25569-80-6			
7	2,4-dichlorobiphenyl	33284-50-3			
8	2,4'-dichlorobiphenyl	34883-43-7	$^{13}C_{12}$-2,4'-dichlorobiphenyl		Recovery Std
9	2,5-dichlorobiphenyl	34883-39-1			
10	2,6-dichlorobiphenyl	33146-45-1			
11	3,3'-dichlorobiphenyl	2050-67-1			
12	3,4-dichlorobiphenyl	2974-92-7			
13	3,4'-dichlorobiphenyl	2974-90-5			
14	3,5-dichlorobiphenyl	34883-41-5			
15	4,4'-dichlorobiphenyl	2050-68-2	$^{13}C_{12}$-4,4'-dichlorobiphenyl		Internal Std
16	2,2',3-trichlorobiphenyl	38444-78-9			
17	2,2',4-trichlorobiphenyl	37680-66-3			
18	2,2',5-trichlorobiphenyl	37680-65-2			
19	2,2',6-trichlorobiphenyl	38444-73-4			
20	2,3,3'-trichlorobiphenyl	38444-84-7			
21	2,3,4-trichlorobiphenyl	55702-46-0			
22	2,3,4'-trichlorobiphenyl	38444-85-8			
23	2,3,5-trichlorobiphenyl	55720-44-0			
24	2,3,6-trichlorobiphenyl	55702-45-9			
25	2,3',4-trichlorobiphenyl	55712-37-3			
26	2,3',5-trichlorobiphenyl	38444-81-4			
27	2,3',6-trichlorobiphenyl	38444-76-7			
28	2,4,4'-trichlorobiphenyl	7012-37-5	$^{13}C_{12}$-2,4,4'-trichlorobiphenyl		Internal Std
29	2,4,5-trichlorobiphenyl	15862-07-4			
30	2,4,6-trichlorobiphenyl	35693-92-6			
31	2,4',5-trichlorobiphenyl	16606-02-3	$^{13}C_{12}$-2,4',5-trichlorobiphenyl		Surrogate Std
32	2,4',6-trichlorobiphenyl	38444-77-8	$^{13}C_{12}$-2,4',6-trichlorobiphenyl		Cleanup Std
33	2',3,4-trichlorobiphenyl (2,3',4'-trichlorobiphenyl)	38444-86-9			
34	2',3,5-trichlorobiphenyl (2,3',5'-trichlorobiphenyl)	37680-68-5			
35	3,3',4-trichlorobiphenyl	37680-69-6			
36	3,3',5-trichlorobiphenyl	38444-87-0			
37	3,4,4'-trichlorobiphenyl	38444-90-5	$^{13}C_{12}$-3,4,4'-trichlorobiphenyl		Recovery Std
38	3,4,5-trichlorobiphenyl	53555-66-1			
39	3,4',5-trichlorobiphenyl	38444-88-1			
40	2,2',3,3'-tetrachlorobiphenyl	38444-93-8			
41	2,2',3,4-tetrachlorobiphenyl	52663-59-9			
42	2,2',3,4'-tetrachlorobiphenyl	36559-22-5			
43	2,2',3,5-tetrachlorobiphenyl	70362-46-8			
44	2,2',3,5'-tetrachlorobiphenyl	41464-39-5			
45	2,2',3,6-tetrachlorobiphenyl	70362-45-7			
46	2,2',3,6'-tetrachlorobiphenyl	41464-47-5			
47	2,2',4,4'-tetrachlorobiphenyl	2437-79-8			
48	2,2',4,5-tetrachlorobiphenyl	70362-47-9			
49	2,2',4,5'-tetrachlorobiphenyl	41464-40-8			
50	2,2',4,6-tetrachlorobiphenyl	62796-65-0			
51	2,2',4,6'-tetrachlorobiphenyl	68194-04-7			
52	2,2',5,5'-tetrachlorobiphenyl	35693-99-3	$^{13}C_{12}$-2,2',5,5'-tetrachlorobiphenyl	160901-66-6	Recovery Std
53	2,2',5,6'-tetrachlorobiphenyl	41464-41-9			
54	2,2',6,6'-tetrachlorobiphenyl	15968-05-5			
55	2,3,3',4-tetrachlorobiphenyl	74338-24-2			

BZ/IUPAC Number[1]	PCB Chemical Structure Name[2]	[redacted]S Registry[3] Number	Labeled Analog	[redacted]S Registry[3]	Usage
56	2,3,3',4'-tetrachlorobiphenyl	41464-43-1			
57	2,3,3',5-tetrachlorobiphenyl	70424-67-8			
58	2,3,3',5'-tetrachlorobiphenyl	41464-49-7			
59	2,3,3',6-tetrachlorobiphenyl	74472-33-6			
60	2,3,4,4'-tetrachlorobiphenyl	33025-41-1			
61	2,3,4,5-tetrachlorobiphenyl	33284-53-6			
62	2,3,4,6-tetrachlorobiphenyl	54230-22-7			
63	2,3,4',5-tetrachlorobiphenyl	74472-34-7			
64	2,3,4',6-tetrachlorobiphenyl	52663-58-8			
65	2,3,5,6-tetrachlorobiphenyl	33284-54-7			
66	2,3',4,4'-tetrachlorobiphenyl	32598-10-0			
67	2,3',4,5-tetrachlorobiphenyl	73575-53-8			
68	2,3',4,5'-tetrachlorobiphenyl	73575-52-7			
69	2,3',4,6-tetrachlorobiphenyl	60233-24-1			
70	2,3',4',5-tetrachlorobiphenyl	32598-11-1			
71	2,3',4',6-tetrachlorobiphenyl	41464-46-4			
72	2,3',5,5'-tetrachlorobiphenyl	41464-42-0			
73	2,3',5',6-tetrachlorobiphenyl	74338-23-1			
74	2,4,4',5-tetrachlorobiphenyl	32690-93-0			
75	2,4,4',6-tetrachlorobiphenyl	32598-12-2			
76	2',3,4,5-tetrachlorobiphenyl (2,3',4',5'-tetrachlorobiphenyl)	70362-48-0			
77	3,3',4,4'-tetrachlorobiphenyl	32598-13-3	$^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl	160901-67-7	Internal Std
78	3,3',4,5-tetrachlorobiphenyl	70362-49-1			
79	3,3',4,5'-tetrachlorobiphenyl	41464-48-6			
80	3,3',5,5'-tetrachlorobiphenyl	33284-52-5			
81	3,4,4',5-tetrachlorobiphenyl	70362-50-4	$^{13}C_{12}$-3,4,4',5-tetrachlorobiphenyl	160901-68-8	Internal Std
82	2,2',3,3',4-pentachlorobiphenyl	52663-62-4			
83	2,2',3,3',5-pentachlorobiphenyl	60145-20-2			
84	2,2',3,3',6-pentachlorobiphenyl	52663-60-2			
85	2,2',3,4,4'-pentachlorobiphenyl	65510-45-4			
86	2,2',3,4,5-pentachlorobiphenyl	55312-69-1			
87	2,2',3,4,5'-pentachlorobiphenyl	38380-02-8			
88	2,2',3,4,6-pentachlorobiphenyl	55215-17-3			
89	2,2',3,4,6'-pentachlorobiphenyl	73575-57-2			
90	2,2',3,4',5-pentachlorobiphenyl	68194-07-0			
91	2,2',3,4',6-pentachlorobiphenyl	68194-05-8			
92	2,2',3,5,5'-pentachlorobiphenyl	52663-61-3			
93	2,2',3,5,6-pentachlorobiphenyl	73575-56-1			
94	2,2',3,5,6'-pentachlorobiphenyl	73575-55-0			
95	2,2',3,5',6-pentachlorobiphenyl	38379-99-6	$^{13}C_{12}$-2,2',3,5',6-pentachlorobiphenyl		Surrogate Std
96	2,2',3,6,6'-pentachlorobiphenyl	73575-54-9			
97	2,2',3',4,5-pentachlorobiphenyl (2,2',3,4',5'-pentachlorobiphenyl)	41464-51-1			
98	2,2',3',4,6-pentachlorobiphenyl (2,2',3,4',6'-pentachlorobiphenyl)	60233-25-2			
99	2,2',4,4',5-pentachlorobiphenyl	38380-01-7			
100	2,2',4,4',6-pentachlorobiphenyl	39485-83-1			
101	2,2',4,5,5'-pentachlorobiphenyl	37680-73-2	$^{13}C_{12}$-2,2',4,5,5'-pentachlorobiphenyl	160901-69-9	Recovery Std
102	2,2',4,5,6-pentachlorobiphenyl	68194-06-9			
103	2,2',4,5',6-pentachlorobiphenyl	60145-21-3			
104	2,2',4,6,6'-pentachlorobiphenyl	56558-16-8			
105	2,3,3',4,4'-pentachlorobiphenyl	32598-14-4	$^{13}C_{12}$-2,3,3',4,4'-pentachlorobiphenyl	160901-70-2	Internal Std
106	2,3,3',4,5-pentachlorobiphenyl	70424-69-0			
107/109	2,3,3',4',5-pentachlorobiphenyl	70424-68-9			
108/107	2,3,3',4,5'-pentachlorobiphenyl	70362-41-3			
109/108	2,3,3',4,6-pentachlorobiphenyl	74472-35-8			
110	2,3,3',4',6-pentachlorobiphenyl	38380-03-9			
111	2,3,3',5,5'-pentachlorobiphenyl	39635-32-0	$^{13}C_{12}$-2,3,3',5,5'-pentachlorobiphenyl	160901-71-3	Cleanup Std
112	2,3,3',5,6-pentachlorobiphenyl	74472-36-9			
113	2,3,3',5',6-pentachlorobiphenyl	68194-10-5			
114	2,3,4,4',5-pentachlorobiphenyl	74472-37-0	$^{13}C_{12}$-2,3,4,4',5-pentachlorobiphenyl	160901-72-4	Internal Std
115	2,3,4,4',6-pentachlorobiphenyl	74472-38-1			

BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number	Labeled Analog	CAS Registry[3]	Usage
116	2,3,4,5,6-pentachlorobiphenyl	18259-05-7			
117	2,3,4',5,6-pentachlorobiphenyl	68194-11-6			
118	2,3',4,4',5-pentachlorobiphenyl	31508-00-6	$^{13}C_{12}$-2,3',4,4',5-pentachlorobiphenyl	160901-73-5	Internal Std
119	2,3',4,4',6-pentachlorobiphenyl	56558-17-9			
120	2,3',4,5,5'-pentachlorobiphenyl	68194-12-7			
121	2,3',4,5',6-pentachlorobiphenyl	56558-18-0			
122	2',3,3',4,5-pentachlorobiphenyl (2,3,3',4',5'-pentachlorobiphenyl)	76842-07-4			
123	2',3,4,4',5-pentachlorobiphenyl (2,3',4,4',5'-pentachlorobiphenyl)	65510-44-3	$^{13}C_{12}$-2',3,4,4',5-pentachlorobiphenyl	160901-74-6	Internal Std
124	2',3,4,5,5'-pentachlorobiphenyl (2,3',4',5',5-pentachlorobiphenyl)	70424-70-3			
125	2',3,4,5,6'-pentachlorobiphenyl (2,3',4',5',6-pentachlorobiphenyl)	74472-39-2			
126	3,3',4,4',5-pentachlorobiphenyl	57465-28-8	$^{13}C_{12}$-3,3',4,4',5-pentachlorobiphenyl	160901-75-7	Internal Std
127	3,3',4,5,5'-pentachlorobiphenyl	39635-33-1			
128	2,2',3,3',4,4'-hexachlorobiphenyl	38380-07-3			
129	2,2',3,3',4,5-hexachlorobiphenyl	55215-18-4			
130	2,2',3,3',4,5'-hexachlorobiphenyl	52663-66-8			
131	2,2',3,3',4,6-hexachlorobiphenyl	61798-70-7			
132	2,2',3,3',4,6'-hexachlorobiphenyl	38380-05-1			
133	2,2',3,3',5,5'-hexachlorobiphenyl	35694-04-3			
134	2,2',3,3',5,6-hexachlorobiphenyl	52704-70-8			
135	2,2',3,3',5,6'-hexachlorobiphenyl	52744-13-5			
136	2,2',3,3',6,6'-hexachlorobiphenyl	38411-22-2			
137	2,2',3,4,4',5-hexachlorobiphenyl	35694-06-5			
138	2,2',3,4,4',5'-hexachlorobiphenyl	35065-28-2	$^{13}C_{12}$-2,2',3,4,4',5'-hexachlorobiphenyl	160901-76-8	Recovery Std
139	2,2',3,4,4',6-hexachlorobiphenyl	56030-56-9			
140	2,2',3,4,4',6'-hexachlorobiphenyl	59291-64-4			
141	2,2',3,4,5,5'-hexachlorobiphenyl	52712-04-6			
142	2,2',3,4,5,6-hexachlorobiphenyl	41411-61-4			
143	2,2',3,4,5,6'-hexachlorobiphenyl	68194-15-0			
144	2,2',3,4,5',6-hexachlorobiphenyl	68194-14-9			
145	2,2',3,4,6,6'-hexachlorobiphenyl	74472-40-5			
146	2,2',3,4',5,5'-hexachlorobiphenyl	51908-16-8			
147	2,2',3,4',5,6-hexachlorobiphenyl	68194-13-8			
148	2,2',3,4',5,6'-hexachlorobiphenyl	74472-41-6			
149	2,2',3,4',5',6-hexachlorobiphenyl	38380-04-0			
150	2,2',3,4',6,6'-hexachlorobiphenyl	68194-08-1			
151	2,2',3,5,5',6-hexachlorobiphenyl	52663-63-5			
152	2,2',3,5,6,6'-hexachlorobiphenyl	68194-09-2			
153	2,2',4,4',5,5'-hexachlorobiphenyl	35065-27-1	$^{13}C_{12}$-2,2',4,4',5,5'-hexachlorobiphenyl		Surrogate Std
154	2,2',4,4',5,6'-hexachlorobiphenyl	60145-22-4			
155	2,2',4,4',6,6'-hexachlorobiphenyl	33979-03-2			
156	2,3,3',4,4',5-hexachlorobiphenyl	38380-08-4	$^{13}C_{12}$-2,3,3',4,4',5-hexachlorobiphenyl	160901-77-9	Internal Std
157	2,3,3',4,4',5'-hexachlorobiphenyl	69782-90-7	$^{13}C_{12}$-2,3,3',4,4',5'-hexachlorobiphenyl	160901-78-0	Internal Std
158	2,3,3',4,4',6-hexachlorobiphenyl	74472-42-7			
159	2,3,3',4,5,5'-hexachlorobiphenyl	39635-35-3			
160	2,3,3',4,5,6-hexachlorobiphenyl	41411-62-5			
161	2,3,3',4,5',6-hexachlorobiphenyl	74472-43-8			
162	2,3,3',4',5,5'-hexachlorobiphenyl	39635-34-2			
163	2,3,3',4',5,6-hexachlorobiphenyl	74472-44-9			
164	2,3,3',4',5',6-hexachlorobiphenyl	74472-45-0			
165	2,3,3',5,5',6-hexachlorobiphenyl	74472-46-1			
166	2,3,4,4',5,6-hexachlorobiphenyl	41411-63-6			
167	2,3',4,4',5,5'-hexachlorobiphenyl	52663-72-6	$^{13}C_{12}$-2,3',4,4',5,5'-hexachlorobiphenyl	161627-18-5	Internal Std
168	2,3',4,4',5',6-hexachlorobiphenyl	59291-65-5			
169	3,3',4,4',5,5'-hexachlorobiphenyl	32774-16-6	$^{13}C_{12}$-3,3',4,4',5,5'-hexachlorobiphenyl	160901-79-1	Internal Std
170	2,2',3,3',4,4',5-heptachlorobiphenyl	35065-30-6	$^{13}C_{12}$-2,2',3,3',4,4',5-heptachlorobiphenyl	160901-80-4	Internal Std
171	2,2',3,3',4,4',6-heptachlorobiphenyl	52663-71-5			
172	2,2',3,3',4,5,5'-heptachlorobiphenyl	52663-74-8			
173	2,2',3,3',4,5,6-heptachlorobiphenyl	68194-16-1			
174	2,2',3,3',4,5,6'-heptachlorobiphenyl	38411-25-5			

BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number	Labeled Analog	CAS Registry[3]	Usage
175	2,2',3,3',4,5',6-heptachlorobiphenyl	40186-70-7			
176	2,2',3,3',4,6,6'-heptachlorobiphenyl	52663-65-7			
177	2,2',3,3',4',5,6-heptachlorobiphenyl (2,2',3,3',4,5',6'-heptachlorobiphenyl)	52663-70-4			
178	2,2',3,3',5,5',6-heptachlorobiphenyl	52663-67-9	$^{13}C_{12}$-2,2',3,3',5,5',6-heptachlorobiphenyl	160901-81-5	Recovery Std
179	2,2',3,3',5,6,6'-heptachlorobiphenyl	52663-64-6			
180	2,2',3,4,4',5,5'-heptachlorobiphenyl	35065-29-3	$^{13}C_{12}$-2,2',3,4,4',5,5'-heptachlorobiphenyl	160901-82-6	Internal Std
181	2,2',3,4,4',5,6-heptachlorobiphenyl	74472-47-2			
182	2,2',3,4,4',5,6'-heptachlorobiphenyl	60145-23-5			
183	2,2',3,4,4',5',6-heptachlorobiphenyl	52663-69-1			
184	2,2',3,4,4',6,6'-heptachlorobiphenyl	74472-48-3			
185	2,2',3,4,5,5',6-heptachlorobiphenyl	52712-05-7			
186	2,2',3,4,5,6,6'-heptachlorobiphenyl	74472-49-4			
187	2,2',3,4',5,5',6-heptachlorobiphenyl	52663-68-0			
188	2,2',3,4',5,6,6'-heptachlorobiphenyl	74487-85-7			
189	2,3,3',4,4',5,5'-heptachlorobiphenyl	39635-31-9	$^{13}C_{12}$-2,3,3',4,4',5,5'-heptachlorobiphenyl	160901-83-7	Internal Std
190	2,3,3',4,4',5,6-heptachlorobiphenyl	41411-64-7			
191	2,3,3',4,4',5',6-heptachlorobiphenyl	74472-50-7			
192	2,3,3',4,5,5',6-heptachlorobiphenyl	74472-51-8			
193	2,3,3',4',5,5',6-heptachlorobiphenyl	69782-91-8			
194	2,2',3,3',4,4',5,5'-octachlorobiphenyl	35694-08-7	$^{13}C_{12}$-2,2',3,3',4,4',5,5'-octachlorobiphenyl		Internal Std
195	2,2',3,3',4,4',5,6-octachlorobiphenyl	52663-78-2			
196	2,2',3,3',4,4',5,6'-octachlorobiphenyl	42740-50-1			
197	2,2',3,3',4,4',6,6'-octachlorobiphenyl	33091-17-7			
198	2,2',3,3',4,5,5',6-octachlorobiphenyl	68194-17-2			
199/200	2,2',3,3',4,5,6,6'-octachlorobiphenyl	52663-73-7			
200/201	2,2',3,3',4,5',6,6'-octachlorobiphenyl	40186-71-8			
201/199	2,2',3,3',4,5,5',6'-octachlorobiphenyl	52663-75-9			
202	2,2',3,3',5,5',6,6'-octachlorobiphenyl	2136-99-4	$^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl		Recovery Std
203	2,2',3,4,4',5,5',6-octachlorobiphenyl	52663-76-0			
204	2,2',3,4,4',5,6,6'-octachlorobiphenyl	74472-52-9			
205	2,3,3',4,4',5,5',6-octachlorobiphenyl	74472-53-0			
206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	40186-72-9	$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-nonachlorobiphenyl		Internal Std
207	2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl	52663-79-3			
208	2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	52663-77-1	$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl		Recovery Std
209	2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	2051-24-3	$^{13}C_{12}$-decachlorobiphenyl	160901-84-8	Internal Std

1. The BZ number is from Ballschmiter and Zell (1980). The IUPAC number, when different from the BZ, follows the recommended changes to the BZ number per Schulte and Malisch (1983) and Guitart et al. (1993).

2. The chemical structure names are from Ballschmiter and Zell (1980). IUPAC nomenclature structure names are listed in parenthesis when different from the BZ name (source CAS Registry).

3. Chemical Abstract Service Registry number (source CAS Registry).

Table 2

Quantitation and Retention Time References Shown With Example Relative Retention Time Windows and Retention Time Limits

IUPAC/BZ	RT Reference	Quantitation Reference	RT	RRT	Window	RT Limit Low	RT Limit High	Ref RT	RRTLimit Low	RRTLimit High
Mono CBs										
3L6	3L6	3L6	15:46	1.000	00:30	15:31	16:01	15:46	0.984	1.016
3L	3L6	3L6	15:45	0.999	00:06	15:42	15:48	15:46	0.996	1.002
1	3L	3L	13:22	0.849	00:10	13:17	13:27	15:45	0.844	0.854
2	3L	3L	15:35	0.989	00:06	15:32	15:38	15:45	0.986	0.992
3	3L	3L	15:46	1.001	00:06	15:43	15:49	15:45	0.998	1.004
Di CBs										
8L	8L	8L	19:07	1.000	00:30	18:52	19:22	19:07	0.987	1.013
15L	8L	8L	22:27	1.174	00:20	22:17	22:37	19:07	1.165	1.183
4	15L	15L	16:07	0.718	00:06	16:04	16:10	22:27	0.716	0.720
10	15L	15L	16:16	0.725	00:06	16:13	16:19	22:26	0.723	0.727
9	15L	15L	18:10	0.809	00:06	18:07	18:13	22:27	0.807	0.811
7	15L	15L	18:19	0.816	00:06	18:16	18:22	22:27	0.814	0.818
6	15L	15L	18:39	0.831	00:06	18:36	18:42	22:27	0.829	0.833
5	15L	15L	19:01	0.847	00:06	18:58	19:04	22:27	0.845	0.849
8	15L	15L	19:08	0.852	00:06	19:05	19:11	22:27	0.850	0.854
14	15L	15L	20:45	0.924	00:06	20:42	20:48	22:27	0.922	0.926
11	15L	15L	21:45	0.969	00:06	21:42	21:48	22:27	0.967	0.971
13	15L	15L	22:06	0.984	00:06	22:03	22:09	22:28	0.982	0.986
12	15L	15L	22:06	0.984	00:06	22:03	22:09	22:28	0.982	0.986
15	15L	15L	22:28	1.001	00:06	22:25	22:31	22:27	0.999	1.003
Tri CBs										
28L	37L	37L	25:30	0.856	00:30	25:15	25:45	29:47	0.848	0.864
37L	37L	37L	29:47	1.000	00:30	29:32	30:02	29:47	0.992	1.008
19	28L	28L	19:33	0.767	00:10	19:28	19:38	25:29	0.764	0.770
30	28L	28L	21:14	0.833	00:06	21:11	21:17	25:29	0.831	0.835
18	28L	28L	21:27	0.841	00:06	21:24	21:30	25:30	0.839	0.843
17	28L	28L	21:52	0.858	00:06	21:49	21:55	25:29	0.856	0.860
27	28L	28L	22:09	0.869	00:06	22:06	22:12	25:29	0.867	0.871
24	28L	28L	22:15	0.873	00:06	22:12	22:18	25:29	0.871	0.875
16	28L	28L	22:29	0.882	00:06	22:26	22:32	25:29	0.880	0.884
32	28L	28L	22:56	0.899	00:06	22:53	22:59	25:31	0.897	0.901
34	28L	28L	24:08	0.946	00:06	24:05	24:11	25:31	0.944	0.948
23	28L	28L	24:15	0.951	00:06	24:12	24:18	25:30	0.949	0.953
29	28L	28L	24:37	0.965	00:10	24:32	24:42	25:31	0.962	0.968
26	28L	28L	24:39	0.967	00:10	24:34	24:44	25:29	0.964	0.970
25	28L	28L	24:54	0.976	00:06	24:51	24:57	25:31	0.974	0.978
31	28L	28L	25:15	0.990	00:06	25:12	25:18	25:30	0.988	0.992
28	28L	28L	25:32	1.001	00:06	25:29	25:35	25:30	0.999	1.003
20	28L	28L	25:41	1.007	00:10	25:36	25:46	25:30	1.004	1.010
21	28L	28L	25:46	1.010	00:06	25:43	25:49	25:31	1.008	1.012
33	28L	28L	25:52	1.014	00:06	25:49	25:55	25:31	1.012	1.016
22	28L	28L	26:18	1.031	00:06	26:15	26:21	25:31	1.029	1.033
36	28L	28L	27:45	1.088	00:06	27:42	27:48	25:30	1.086	1.090
39	28L	28L	28:10	1.105	00:06	28:07	28:13	25:29	1.103	1.107
38	28L	28L	28:47	1.129	00:06	28:44	28:50	25:30	1.127	1.131
35	28L	28L	29:21	1.151	00:06	29:18	29:24	25:30	1.149	1.153
37	28L	28L	29:48	1.169	00:06	29:45	29:51	25:30	1.167	1.171
Tetra CBs										
52L	52L	52L	27:26	1.000	00:30	27:11	27:41	27:26	0.991	1.009
81L	52L	52L	27:26	1.000	00:20	27:16	27:36	27:26	0.994	1.006
77L	52L	52L	37:14	1.357	00:20	37:04	37:24	27:26	1.351	1.363
54	77L	77L	22:54	0.615	00:10	22:49	22:59	37:14	0.613	0.617
50	77L	77L	24:56	0.670	00:10	24:51	25:01	37:13	0.668	0.672
53	77L	77L	25:04	0.673	00:10	24:59	25:09	37:15	0.671	0.675
51	77L	77L	25:47	0.692	00:10	25:42	25:52	37:16	0.690	0.694
45	77L	77L	25:47	0.692	00:10	25:42	25:52	37:16	0.690	0.694
46	77L	77L	26:11	0.703	00:06	26:08	26:14	37:15	0.702	0.704
52	77L	77L	27:28	0.738	00:06	27:25	27:31	37:13	0.737	0.739
73	77L	77L	27:34	0.740	00:06	27:31	27:37	37:15	0.739	0.741

Quantitation and Retention Time References Shown With Example Relative Retention Time Windows and Retention Time Limits

IUPAC/BZ	RT Reference	Quantitation Reference	RT	RRT	Window	RT Limit Low	RT Limit High	Ref RT	RRTLimit Low	RRTLimit High
43	77L	77L	27:40	0.743	00:06	27:37	27:43	37:14	0.742	0.744
69	77L	77L	27:46	0.746	00:10	27:41	27:51	37:13	0.744	0.748
49	77L	77L	27:55	0.750	00:10	27:50	28:00	37:13	0.748	0.752
48	77L	77L	28:12	0.757	00:06	28:09	28:15	37:15	0.756	0.758
65	77L	77L	28:26	0.764	00:10	28:21	28:31	37:13	0.762	0.766
47	77L	77L	28:26	0.764	00:10	28:21	28:31	37:13	0.762	0.766
44	77L	77L	28:34	0.767	00:10	28:29	28:39	37:15	0.765	0.769
62	77L	77L	28:42	0.771	00:10	28:37	28:47	37:13	0.769	0.773
75	77L	77L	28:42	0.771	00:10	28:37	28:47	37:13	0.769	0.773
59	77L	77L	28:52	0.775	00:10	28:47	28:57	37:15	0.773	0.777
42	77L	77L	29:05	0.781	00:06	29:02	29:08	37:14	0.780	0.782
41	77L	77L	29:31	0.793	00:10	29:26	29:36	37:13	0.791	0.795
71	77L	77L	29:35	0.795	00:10	29:30	29:40	37:13	0.793	0.797
40	77L	77L	29:45	0.799	00:10	29:40	29:50	37:14	0.797	0.801
64	77L	77L	29:48	0.800	00:06	29:45	29:51	37:15	0.799	0.801
72	77L	77L	30:28	0.818	00:06	30:25	30:31	37:15	0.817	0.819
68	77L	77L	30:45	0.826	00:06	30:42	30:48	37:14	0.825	0.827
57	77L	77L	31:14	0.839	00:06	31:11	31:17	37:14	0.838	0.840
58	77L	77L	31:33	0.847	00:06	31:30	31:36	37:15	0.846	0.848
67	77L	77L	31:39	0.850	00:06	31:36	31:42	37:14	0.849	0.851
63	77L	77L	31:56	0.858	00:06	31:53	31:59	37:13	0.857	0.859
61	77L	77L	32:10	0.864	00:12	32:04	32:16	37:14	0.861	0.867
74	77L	77L	32:20	0.868	00:12	32:14	32:26	37:15	0.865	0.871
76	77L	77L	32:20	0.868	00:12	32:14	32:26	37:15	0.865	0.871
70	77L	77L	32:20	0.868	00:12	32:14	32:26	37:15	0.865	0.871
66	77L	77L	32:40	0.877	00:06	32:37	32:43	37:15	0.876	0.878
55	77L	77L	32:55	0.884	00:06	32:52	32:58	37:14	0.883	0.885
56	77L	77L	33:28	0.899	00:06	33:25	33:31	37:14	0.898	0.900
60	77L	77L	33:39	0.904	00:06	33:36	33:42	37:13	0.903	0.905
80	77L	77L	33:48	0.908	00:06	33:45	33:51	37:13	0.907	0.909
79	77L	77L	35:30	0.953	00:06	35:27	35:33	37:15	0.952	0.954
78	77L	77L	36:06	0.970	00:06	36:03	36:09	37:13	0.969	0.971
81	81L	81L	36:36	0.983	00:06	36:33	36:39	37:14	0.982	0.984
77	77L	77L	37:15	1.000	00:06	37:12	37:18	37:15	0.999	1.001
Penta CBs										
101L	101L	101L	34:19	1.000	00:20	34:09	34:29	34:19	0.995	1.005
123L	101L	101L	39:02	1.137	00:20	38:52	39:12	34:20	1.132	1.142
118L	101L	101L	39:21	1.147	00:20	39:11	39:31	34:18	1.142	1.152
114L	101L	101L	39:55	1.163	00:20	39:45	40:05	34:19	1.158	1.168
105L	101L	101L	40:43	1.186	00:20	40:33	40:53	34:20	1.181	1.191
126L	101L	101L	43:46	1.275	00:20	43:36	43:56	34:20	1.270	1.280
104	123L	PeL	28:24	0.728	00:10	28:19	28:29	39:01	0.726	0.730
96	123L	PeL	28:59	0.743	00:10	28:54	29:04	39:01	0.741	0.745
103	123L	PeL	30:39	0.785	00:06	30:36	30:42	39:03	0.784	0.786
94	123L	PeL	31:01	0.795	00:06	30:58	31:04	39:01	0.794	0.796
100	123L	PeL	31:30	0.807	00:10	31:25	31:35	39:02	0.805	0.809
95	123L	PeL	31:30	0.807	00:10	31:25	31:35	39:02	0.805	0.809
93	123L	PeL	31:42	0.812	00:10	31:37	31:47	39:02	0.810	0.814
102	123L	PeL	31:51	0.816	00:10	31:46	31:56	39:02	0.814	0.818
98	123L	PeL	31:51	0.816	00:10	31:46	31:56	39:02	0.814	0.818
88	123L	PeL	32:13	0.825	00:12	32:07	32:19	39:03	0.822	0.828
91	123L	PeL	32:22	0.829	00:10	32:17	32:27	39:03	0.827	0.831
84	123L	PeL	32:44	0.839	00:06	32:41	32:47	39:01	0.838	0.840
89	123L	PeL	33:12	0.851	00:06	33:09	33:15	39:01	0.850	0.852
121	123L	PeL	33:12	0.851	00:06	33:09	33:15	39:01	0.850	0.852
92	123L	PeL	33:46	0.865	00:06	33:43	33:49	39:02	0.864	0.866
113	123L	PeL	34:19	0.879	00:10	34:14	34:24	39:02	0.877	0.881
90	123L	PeL	34:19	0.879	00:10	34:14	34:24	39:02	0.877	0.881
101	123L	PeL	34:19	0.879	00:10	34:14	34:24	39:02	0.877	0.881
99	123L	PeL	34:54	0.894	00:12	34:48	35:00	39:02	0.891	0.897
83	123L	PeL	34:54	0.894	00:12	34:48	35:00	39:02	0.891	0.897
112	123L	PeL	35:05	0.899	00:06	35:02	35:08	39:01	0.898	0.900

Quantitation and Retention Time References Shown With Example Relative Retention Time Windows and Retention Time Limits

IUPAC/BZ	RT Reference	Quantitation Reference	RT	RRT	Window	RT Limit Low	RT Limit High	Ref RT	RRTLimit Low	RRTLimit High
119	123L	PeL	35:24	0.907	00:16	35:16	35:32	39:02	0.904	0.910
108U/109B	123L	PeL	35:24	0.907	00:16	35:16	35:32	39:02	0.904	0.910
86	123L	PeL	35:32	0.910	00:16	35:24	35:40	39:03	0.907	0.913
97	123L	PeL	35:32	0.910	00:16	35:24	35:40	39:03	0.907	0.913
125	123L	PeL	35:38	0.913	00:16	35:30	35:46	39:02	0.910	0.916
87	123L	PeL	35:41	0.914	00:10	35:36	35:46	39:02	0.912	0.916
117	123L	PeL	36:06	0.925	00:12	36:00	36:12	39:02	0.922	0.928
116	123L	PeL	36:10	0.927	00:12	36:04	36:16	39:01	0.924	0.930
85	123L	PeL	36:18	0.930	00:10	36:13	36:23	39:02	0.928	0.932
115	123L	PeL	36:25	0.933	00:10	36:20	36:30	39:02	0.931	0.935
110	123L	PeL	36:29	0.935	00:10	36:24	36:34	39:01	0.933	0.937
82	123L	PeL	36:56	0.946	00:06	36:53	36:59	39:02	0.945	0.947
111	123L	PeL	36:56	0.946	00:06	36:53	36:59	39:02	0.945	0.947
120	123L	PeL	37:24	0.958	00:06	37:21	37:27	39:02	0.957	0.959
124	123L	PeL	38:42	0.991	00:10	38:37	38:47	39:03	0.989	0.993
107U/108B	123L	PeL	38:42	0.991	00:10	38:37	38:47	39:03	0.989	0.993
109U/107B	123L	PeL	38:56	0.997	00:06	38:53	38:59	39:03	0.996	0.998
123	123L	123L	39:03	1.000	00:06	39:00	39:06	39:03	0.999	1.001
106	123L	PeL	39:12	1.004	00:06	39:09	39:15	39:03	1.003	1.005
118	118L	118L	39:24	1.001	00:06	39:21	39:27	39:22	1.000	1.002
122	123L	PeL	39:51	1.021	00:06	39:48	39:54	39:02	1.020	1.022
114	114L	114L	39:57	1.001	00:06	39:54	40:00	39:55	1.000	1.002
105	105L	105L	40:44	1.000	00:06	40:41	40:47	40:44	0.999	1.001
127	123L	PeL	42:01	1.076	00:06	41:58	42:04	39:03	1.075	1.077
126	126L	126L	43:47	1.000	00:06	43:44	43:50	43:47	0.999	1.001
Hexa CBs										
138L	138L	138L	42:31	1.000	00:30	42:16	42:46	42:31	0.994	1.006
167L	138L	138L	45:27	1.069	00:20	45:17	45:37	42:31	1.065	1.073
156L	138L	138L	46:41	1.098	00:20	46:31	46:51	42:31	1.094	1.102
157L	138L	138L	46:47	1.100	00:06	46:44	46:50	42:32	1.099	1.101
169L	138L	138L	49:58	1.175	00:20	49:48	50:08	42:31	1.171	1.179
155	167L	HxL	33:55	0.746	00:10	33:50	34:00	45:28	0.744	0.748
152	167L	HxL	34:27	0.758	00:06	34:24	34:30	45:27	0.757	0.759
150	167L	HxL	34:29	0.759	00:06	34:26	34:32	45:26	0.758	0.760
136	167L	HxL	35:06	0.772	00:06	35:03	35:09	45:28	0.771	0.773
145	167L	HxL	35:14	0.775	00:06	35:11	35:17	45:28	0.774	0.776
148	167L	HxL	36:31	0.803	00:06	36:28	36:34	45:29	0.802	0.804
151	167L	HxL	37:17	0.820	00:10	37:12	37:22	45:28	0.818	0.822
154	167L	HxL	37:23	0.823	00:10	37:18	37:28	45:25	0.821	0.825
135	167L	HxL	37:23	0.823	00:10	37:18	37:28	45:25	0.821	0.825
144	167L	HxL	37:51	0.833	00:06	37:48	37:54	45:26	0.832	0.834
147	167L	HxL	38:13	0.841	00:10	38:08	38:18	45:27	0.839	0.843
149	167L	HxL	38:15	0.842	00:10	38:10	38:20	45:26	0.840	0.844
134	167L	HxL	38:32	0.848	00:10	38:27	38:37	45:26	0.846	0.850
143	167L	HxL	38:36	0.849	00:10	38:31	38:41	45:28	0.847	0.851
139	167L	HxL	38:46	0.853	00:10	38:41	38:51	45:27	0.851	0.855
140	167L	HxL	38:49	0.854	00:10	38:44	38:54	45:27	0.852	0.856
131	167L	HxL	39:07	0.861	00:06	39:04	39:10	45:26	0.860	0.862
142	167L	HxL	39:15	0.864	00:06	39:12	39:18	45:26	0.863	0.865
132	167L	HxL	39:40	0.873	00:10	39:35	39:45	45:26	0.871	0.875
133	167L	HxL	39:53	0.878	00:06	39:50	39:56	45:26	0.877	0.879
165	167L	HxL	40:16	0.886	00:06	40:13	40:19	45:27	0.885	0.887
146	167L	HxL	40:32	0.892	00:06	40:29	40:35	45:26	0.891	0.893
161	167L	HxL	40:38	0.894	00:06	40:35	40:41	45:27	0.893	0.895
153	167L	HxL	41:09	0.905	00:10	41:04	41:14	45:28	0.903	0.907
168	167L	HxL	41:09	0.905	00:10	41:04	41:14	45:28	0.903	0.907
141	167L	HxL	41:28	0.912	00:06	41:25	41:31	45:28	0.911	0.913
130	167L	HxL	41:55	0.922	00:06	41:52	41:58	45:28	0.921	0.923
137	167L	HxL	42:04	0.926	00:06	42:01	42:07	45:26	0.925	0.927
164	167L	HxL	42:16	0.930	00:06	42:13	42:19	45:27	0.929	0.931
163	167L	HxL	42:33	0.936	00:06	42:30	42:36	45:28	0.935	0.937
138	167L	HxL	42:33	0.936	00:14	42:26	42:40	45:28	0.933	0.939

Quantitation and Retention Time References Shown With Example Relative Retention Time Windows and Retention Time Limits

IUPAC/BZ	RT Reference	Quantitation Reference	RT	RRT	Window	RT Limit Low	RT Limit High	Ref RT	RRTLimit Low	RRTLimit High
129	167L	HxL	42:41	0.939	00:14	42:34	42:48	45:27	0.936	0.942
160	167L	HxL	42:41	0.939	00:14	42:34	42:48	45:27	0.936	0.942
158	167L	HxL	42:54	0.944	00:06	42:51	42:57	45:27	0.943	0.945
166	167L	HxL	43:44	0.962	00:10	43:39	43:49	45:28	0.960	0.964
128	167L	HxL	43:58	0.967	00:10	43:53	44:03	45:28	0.965	0.969
159	167L	HxL	44:40	0.983	00:06	44:37	44:43	45:26	0.982	0.984
162	167L	HxL	44:59	0.990	00:06	44:56	45:02	45:26	0.989	0.991
167	167L	167L	45:28	1.000	00:06	45:25	45:31	45:28	0.999	1.001
156	156L	156L	46:42	1.000	00:06	46:39	46:45	46:42	0.999	1.001
157	157L	157L	46:49	1.001	00:10	46:44	46:54	46:46	0.999	1.003
169	169L	169L	49:59	1.000	00:06	49:56	50:02	49:59	0.999	1.001
Hepta CBs										
178L	178L	178L	42:50	1.000	00:30	42:35	43:05	42:50	0.994	1.006
180L	178L	178L	47:58	1.120	00:20	47:48	48:08	42:50	1.116	1.124
170L	178L	178L	49:22	1.153	00:20	49:12	49:32	42:49	1.149	1.157
189L	178L	178L	52:24	1.223	00:20	52:14	52:34	42:51	1.219	1.227
188	180L	HpL	39:44	0.828	00:06	39:41	39:47	47:59	0.827	0.829
179	180L	HpL	40:17	0.840	00:06	40:14	40:20	47:57	0.839	0.841
184	180L	HpL	40:35	0.846	00:06	40:32	40:38	47:58	0.845	0.847
176	180L	HpL	41:09	0.858	00:06	41:06	41:12	47:58	0.857	0.859
186	180L	HpL	41:39	0.868	00:06	41:36	41:42	47:59	0.867	0.869
178	180L	HpL	42:52	0.894	00:06	42:49	42:55	47:57	0.893	0.895
175	180L	HpL	43:28	0.906	00:06	43:25	43:31	47:59	0.905	0.907
187	180L	HpL	43:45	0.912	00:06	43:42	43:48	47:58	0.911	0.913
182	180L	HpL	43:55	0.916	00:06	43:52	43:58	47:57	0.915	0.917
183	180L	HpL	44:20	0.924	00:06	44:17	44:23	47:59	0.923	0.925
185	180L	HpL	44:34	0.929	00:06	44:31	44:37	47:58	0.928	0.930
174	180L	HpL	44:47	0.934	00:06	44:44	44:50	47:57	0.933	0.935
177	180L	HpL	45:12	0.942	00:06	45:09	45:15	47:59	0.941	0.943
181	180L	HpL	45:30	0.949	00:06	45:27	45:33	47:57	0.948	0.950
171	180L	HpL	45:49	0.955	00:10	45:44	45:54	47:59	0.953	0.957
173	180L	HpL	45:49	0.955	00:06	45:46	45:52	47:59	0.954	0.956
172	180L	HpL	47:20	0.987	00:06	47:17	47:23	47:57	0.986	0.988
192	180L	HpL	47:35	0.992	00:06	47:32	47:38	47:58	0.991	0.993
193	180L	HpL	47:58	1.000	00:06	47:55	48:01	47:58	0.999	1.001
180	180L	180L	47:58	1.000	00:06	47:55	48:01	47:58	0.999	1.001
191	180L	HpL	48:20	1.008	00:06	48:17	48:23	47:57	1.007	1.009
170	170L	170L	49:23	1.000	00:06	49:20	49:26	49:23	0.999	1.001
190	180L	HpL	49:52	1.040	00:06	49:49	49:55	47:57	1.039	1.041
189	189L	189L	52:26	1.001	00:06	52:23	52:29	52:23	1.000	1.002
Octa CBs										
202L	202L	202L	45:08	1.000	00:30	44:53	45:23	45:08	0.994	1.006
194L	202L	202L	54:29	1.207	00:20	54:19	54:39	45:08	1.203	1.211
202	194L	194L	45:10	0.829	00:10	45:05	45:15	54:29	0.827	0.831
201U/200B	194L	194L	46:03	0.845	00:10	45:58	46:08	54:30	0.843	0.847
204	194L	194L	46:41	0.857	00:06	46:38	46:44	54:28	0.856	0.858
197	194L	194L	46:57	0.862	00:10	46:52	47:02	54:28	0.860	0.864
200U/199B	194L	194L	47:13	0.867	00:06	47:10	47:16	54:28	0.866	0.868
198	194L	194L	49:52	0.915	00:06	49:49	49:55	54:30	0.914	0.916
199U/201B	194L	194L	49:55	0.916	00:06	49:52	49:58	54:30	0.915	0.917
196	194L	194L	50:34	0.928	00:06	50:31	50:37	54:29	0.927	0.929
203	194L	194L	50:45	0.931	00:06	50:42	50:48	54:31	0.930	0.932
195	194L	194L	52:14	0.959	00:06	52:11	52:17	54:28	0.958	0.960
194	194L	194L	54:30	1.000	00:06	54:27	54:33	54:30	0.999	1.001
205	194L	194L	54:57	1.009	00:06	54:54	55:00	54:28	1.008	1.010
Nona CBs										
208L	208L	208L	51:46	1.000	00:30	51:31	52:01	51:46	0.995	1.005
206L	208L	208L	56:37	1.094	00:20	56:27	56:47	51:45	1.091	1.097
208	206L	206L	51:47	0.915	00:06	51:44	51:50	56:36	0.914	0.916
207	206L	206L	52:42	0.931	00:06	52:39	52:45	56:36	0.930	0.932
206	206L	206L	56:39	1.001	00:06	56:36	56:42	56:36	1.000	1.002
Deca CBs										

Quantitation and Retention Time References Shown With Example Relative Retention Time Windows and Retention Time Limits

IUPAC/BZ	RT Reference	Quantitation Reference	RT	RRT	Window	RT Limit Low	RT Limit High	Ref RT	RRTLimit Low	RRTLimit High
209L	208L	208L	58:06	1.122	00:30	57:51	58:21	51:47	1.117	1.127
209	209L	209L	58:08	1.001	00:06	58:05	58:11	58:05	1.000	1.002
Cleanup	**Standards**									
32L	37L	37L	22:57	0.771	00:20	22:47	23:07	29:47	0.765	0.776
111L	101L	101L	36:55	1.0758	00:20	36:45	37:05	34:19	1.071	1.081
Sampling	**Surrogates**									
31L	28L	28L	25:14	0.9895	00:20	25:04	25:24	25:30	0.983	0.996
95L	123L	123L	31:31	0.8074	00:20	31:21	31:41	39:02	0.803	0.812
153L	167L	167L	41:07	0.9047	00:20	40:57	41:17	45:27	0.901	0.908

Table 3

Low Calibration Levels Based on Various Final Extract Volumes

(20µL and 100µL)

Analyte	Extract Low Cal. level (ng/mL)	Extract Vol.(mL)	Water 1L (ng/L)	Solid 10g (ng/g)	Extract Vol. (mL)	Water 1L (ng/L)	Solid 10g (ng/g)
Monochlorobiphenyls	0.2	0.02	0.004[1]	0.0004[1]	0.1	0.02	0.002
Dichlorobiphenyls	0.2	0.02	0.004[1]	0.0004[1]	0.1	0.02	0.002
Trichlorobiphenyls	0.2	0.02	0.004	0.0004	0.1	0.02	0.002
Tetrachlorobiphenyls	0.2	0.02	0.004	0.0004	0.1	0.02	0.002
Pentachlorobiphenyls	0.2	0.02	0.004	0.0004	0.1	0.02	0.002
Hexachlorobiphenyls	0.2	0.02	0.004	0.0004	0.1	0.02	0.002
Heptachlorobiphenyls	0.2	0.02	0.004	0.0004	0.1	0.02	0.002
Octachlorobiphenyls	0.2	0.02	0.004	0.0004	0.1	0.02	0.002
Nonachlorobiphenyls	0.2	0.02	0.004	0.0004	0.1	0.02	0.002
Decachlorobiphenyl	0.2	0.02	0.004	0.0004	0.1	0.02	0.002

1. This value reflects the lower calibration level. Reliable detection at this level may not be attained due to evaporative loss in adjusting the extract volume to 20 µL.

Table 4

Estimated Minimum Levels – Matrix and Concentration

Analyte	Extract Vol. (µL)	Water 1L (ng/L)	Solid 10g (ng/g)	Wipes, Solid 1.0g (ng/sample)
Monochlorobiphenyls	100	0.25	0.025	0.25
Dichlorobiphenyls	100	0.25	0.025	0.25
Trichlorobiphenyls	100	0.25	0.025	0.25
Tetrachlorobiphenyls	100	0.25	0.025	0.25
Pentachlorobiphenyls	100	0.25	0.025	0.25
Hexachlorobiphenyls	100	0.25	0.025	0.25
Heptachlorobiphenyls	100	0.25	0.025	0.25
Octachlorobiphenyls	100	0.25	0.025	0.25
Nonachlorobiphenyls	100	0.25	0.025	0.25
Decachlorobiphenyl	100	0.25	0.025	0.25

The estimated minimum level (EML) is defined as the lowest concentration at which an analyte can be measured reliably with common laboratory interferences present assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures. Deviations from the extraction amounts or final volumes listed will result in corresponding changes in the actual sample ML.

These EMLs differ from those listed in the reference method. The EMLs provided are based on historical blank data and calibration data obtained while performing EPA 1668mod. The survey period was approximately 2 years. During this period, blank contamination in excess of the minimum levels was rare.

Table 5

Concentration of Stock and Spiking Solutions Containing PCBs and Labeled Compounds

PCB Congener	BZ/ IUPAC	Standard Source	Catalog Number	Solution concentration (ng/mL) Labeled compound Stock[1]	Labeled compound Spiking[2]	PAR Stock[3]	PAR Spiking[4]
2-MoCB	1	AccuStd	C-001S TP	---	---	3000	5.0
4-MoCB	3	AccuStd	C-003S TP	---	---	3000	5.0
2,2'-DiCB	4	AccuStd	C-004S TP	---	---	3000	5.0
4,4'-DiCB	15	AccuStd	C-015S TP	---	---	3000	5.0
2,2',6-TrCB	19	AccuStd	C-019S TP	---	---	3000	5.0
3,4,4'-TrCB	37	AccuStd	C-037S TP	---	---	3000	5.0
2,2',6,6'-TeCB	54	AccuStd	C-054S TP	---	---	3000	5.0
3,3',4,4'-TeCB	77	AccuStd	C-077S TP	---	---	3000	5.0
3,4,4',5-TeCB	81	AccuStd	C-081S TP	---	---	3000	5.0
2,2',4,6,6'-PeCB	104	AccuStd	C-104S TP	---	---	3000	5.0
2,3,3',4,4'-PeCB	105	AccuStd	C-105S TP	---	---	3000	5.0
2,3,4,4',5-PeCB	114	AccuStd	C-114S TP	---	---	3000	5.0
2,3',4,4',5-PeCB	118	AccuStd	C-118S TP	---	---	3000	5.0
2',3,4,4',5-PeCB	123	AccuStd	C-123S TP	---	---	3000	5.0
3,3',4,4',5-PeCB	126	AccuStd	C-126S TP	---	---	3000	5.0
2,2',4,4',6,6'-HxCB	155	AccuStd	C-155S TP	---	---	3000	5.0
2,3,3',4,4',5-HxCB	156	AccuStd	C-156S TP	---	---	3000	5.0
2,3,3',4,4',5'-HxCB	157	AccuStd	C-157S TP	---	---	3000	5.0
2,3',4,4',5,5'-HxCB	167	AccuStd	C-167S TP	---	---	3000	5.0
3,3',4,4',5,5'-HxCB	169	AccuStd	C-169S TP	---	---	3000	5.0
2,2',3,3',4,4',5-HpCB	170	AccuStd	C-170S TP	---	---	3000	5.0
2,2',3,4,4',5,5'-HpCB	180	AccuStd	C-180S TP	---	---	3000	5.0
2,2',3,4',5,6,6'-HpCB	188	AccuStd	C-188S TP	---	---	3000	5.0
2,3,3',4,4',5,5'-HpCB	189	AccuStd	C-189S TP	---	---	3000	5.0
2,2',3,3',5,5',6,6'-OcCB	202	AccuStd	C-202S TP	---	---	3000	5.0
2,3,3',4,4',5,5',6-OcCB	205	AccuStd	C-205S TP	---	---	3000	5.0
2,2',3,3',4,4',5,5',6-NoCB	206	AccuStd	C-206S TP	---	---	3000	5.0
2,2',3,3',4',5,5',6,6'-NoCB	208	AccuStd	C-208S TP	---	---	3000	5.0
DeCB	209	AccuStd	C-209S TP	---	---	3000	5.0
Labeled Internal Standards							
$^{13}C_{12}$-4-chlorobiphenyl	$3L_{12}$	Wellington	MBP-3	1000	10	---	---
$^{13}C_{12}$-4,4'-dichlorobiphenyl	15L	Cambridge	EC-1402	1000	10	---	---
$^{13}C_{12}$-2,4,4`-trichlorobiphenyl	28L	Cambridge	EC-1413	1000	10	---	---
$^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl	77L	Cambridge	EC-1404	1000	10	---	---
$^{13}C_{12}$-3,4,4',5-tetrachlorobiphenyl	81L	Cambridge	EC-1412	1000	10	---	---
$^{13}C_{12}$-2,3,3',4,4'-pentachlorobiphenyl	105L	Cambridge	EC-1420	1000	10	---	---
$^{13}C_{12}$2,3,4,4',5-pentachlorobiphenyl -	114L	Wellington	MBP-114	1000	10	---	---
$^{13}C_{12}$-2,3',4,4',5-pentachlorobiphenyl	118L	Cambridge	EC-1435	1000	10	---	---
$^{13}C_{12}$-2',3,4,4',5-pentachlorobiphenyl	123L	Wellington	MBP-123	1000	10	---	---
$^{13}C_{12}$-3,3',4,4',5-pentachlorobiphenyl	126L	Cambridge	EC-1425	1000	10	---	---
$^{13}C_{12}$-2,3,3',4,4',5-hexachlorobiphenyl	156L	Cambridge	EC-1422	1000	10	---	---
$^{13}C_{12}$-2,3,3',4,4',5'-hexachlorobiphenyl	157L	Cambridge	EC-4051	1000	10	---	---
$^{13}C_{12}$-2,3',4,4',5,5'-hexachlorobiphenyl	167L	Cambridge	EC-4050	1000	10	---	---
$^{13}C_{12}$-3,3',4,4',5,5'-hexachlorobiphenyl	169L	Cambridge	EC-1416	1000	10	---	---
$^{13}C_{12}$-2,2',3,3',4,4',5-heptachlorobiphenyl	170L	Wellington	MBP-170	1000	10	---	---
$^{13}C_{12}$-2,2',3,4,4',5,5'-heptachlorobiphenyl	180L	Cambridge	EC-1407	1000	10	---	---
$^{13}C_{12}$-2,3,3',4,4',5,5'-heptachlorobiphenyl	189L	Cambridge	EC-1409	1000	10	---	---
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-octachlorobiphenyl	194L	Cambridge	EC-1418	1000	10	---	---
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	206L	Wellington	MBP-206	1000	10	---	---
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	209L	Cambridge	EC-1410	1000	10	---	---

Table 5 Continued

PCB Congener	BZ/ IUPAC	Standard Source	Catalog Number	Solution concentration (ng/mL) Labeled compound Stock[1]	Labeled compound Spiking[2]	PAR Stock[3]	PAR Spiking[4]
Labeled Recovery Standards[5]							
$^{13}C_6$-4-chlorobiphenyl	$3L_6$	Cambridge	EC-1401	1000	100		
$^{13}C_{12}$-2,4'-dichlorobiphenyl	8L	Wellington	MBP-8	1000	100		
$^{13}C_{12}$-3,4,4'-trichlorobiphenyl	37L	Wellington	MBP-37	1000	100		
$^{13}C_{12}$-2,2',5,5'-tetrachlorobiphenyl	52L	Cambridge	EC-1424	1000	100		
$^{13}C_{12}$-2,2',4,5,5'-pentachlorobiphenyl	101L	Cambridge	EC-1405	1000	100		
$^{13}C_{12}$-2,2',3,4,4',5'-hexachlorobiphenyl	138L	Cambridge	EC-1436	1000	100		
$^{13}C_{12}$-2,2',3,3',5,5',6-heptachlorobiphenyl	178L	Cambridge	EC-1417	1000	100		
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl	202L	Cambridge	EC-1408	1000	100		
$^{13}C_{12}$-2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	208L	Cambridge	EC-1419	1000	100		
Cleanup Standards[6]							
$^{13}C_{12}$-3,4,4',5-tetrachlorobiphenyl	32L	Cambridge	EC-4163	5000	10		
$^{13}C_{12}$-2,3,3',5,5'-pentachlorobiphenyl	111L	Cambridge	EC-1415	5000	10		
Labeled Surrogate Standards[7]							
$^{13}C_{12}$-2,4',5-trichlorobiphenyl	31L	Wellington	MBP-31	5000	50		
$^{13}C_{12}$-2,2',3,5',6-pentachlorobiphenyl	95L	Wellington	MBP-95	5000	50		
$^{13}C_{12}$-2,2',4,4',5,5'-hexachlorobiphenyl	153L	Wellington	MBP-153	5000	50		

Notes:

1. Section 7.12.4.3– prepared in nonane and diluted to prepare spiking solution
2. Section 7.12.8– prepared in acetone from stock solution.
3. Section 7.12.4.1 – prepared in nonane and diluted to prepare spiking solution.
4. Section 7.12.7– prepared in acetone from stock solution.
5. Section 7.12.9– prepared in hexane and added to extract prior to cleanup.
6. Section 7.12.11– prepared in nonane and added to concentrated extract prior to injection.
7. Section 7.12.10– prepared in nonane and added to XAD tube prior to sampling.

Table 6

Concentration of PCBs in Calibration Verification Solutions

Congeners		CS 0.2 ng/mL	CS 1 ng/mL	CS 2 ng/mL	CS 3 ng/mL	CS 4 ng/mL	CS 5 ng/mL
2-MoCB	1	0.2	1.0	5.0	50	400	2000
4-MoCB	3	0.2	1.0	5.0	50	400	2000
2,2'-DiCB	4	0.2	1.0	5.0	50	400	2000
4,4'-DiCB	15	0.2	1.0	5.0	50	400	2000
2,2',6'-TrCB	19	0.2	1.0	5.0	50	400	2000
3,4,4'-TrCB	37	0.2	1.0	5.0	50	400	2000
2,2',6,6'-TeCB	54	0.2	1.0	5.0	50	400	2000
3,3',4,4'-TeCB	77	0.2	1.0	5.0	50	400	2000
3,4,4',5-TeCB	81	0.2	1.0	5.0	50	400	2000
2,2',4,6,6'-PeCB	104	0.2	1.0	5.0	50	400	2000
2,3,3',4,4'-PeCB	105	0.2	1.0	5.0	50	400	2000
2,3,4,4',5-PeCB	114	0.2	1.0	5.0	50	400	2000
2,3',4,4',5-PeCB	118	0.2	1.0	5.0	50	400	2000
2',3,4,4',5-PeCB	123	0.2	1.0	5.0	50	400	2000
3,3',4,4',5-PeCB	126	0.2	1.0	5.0	50	400	2000
2,2',4,4',6,6'-HxCB	155	0.2	1.0	5.0	50	400	2000
2,3,3',4,4',5-HxCB	156	0.2	1.0	5.0	50	400	2000
2,3,3',4,4',5'-HxCB	157	0.2	1.0	5.0	50	400	2000
2,3',4,4',5,5'-HxCB	167	0.2	1.0	5.0	50	400	2000
3,3',4,4',5,5'-HxCB	169	0.2	1.0	5.0	50	400	2000
2,2',3,3',4,4',5-HpCB	170	0.2	1.0	5.0	50	400	2000
2,2',3,4,4',5,5'-HpCB	180	0.2	1.0	5.0	50	400	2000
2,2',3,4',5,6,6'-HpCB	188	0.2	1.0	5.0	50	400	2000
2,3,3',4,4',5,5'-HpCB	189	0.2	1.0	5.0	50	400	2000
2,2',3,3',5,5',6,6'-OcCB	202	0.2	1.0	5.0	50	400	2000
2,3,3',4,4',5,5',6-OcCB	205	0.2	1.0	5.0	50	400	2000
2,2',3,3',4,4',5,5',6-NoCB	206	0.2	1.0	5.0	50	400	2000
2,2',3,3',4',5,5',6,6'-NoCB	208	0.2	1.0	5.0	50	400	2000
DeCB	209	0.2	1.0	5.0	50	400	2000
Labeled Congeners							
$^{13}C_{12}$-4-MoCB	3L	100	100	100	100	100	100
$^{13}C_{12}$-4,4'-DiCB	15L	100	100	100	100	100	100
$^{13}C_{12}$-2,4,4'-TrCB	28L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4'-TeCB	77L	100	100	100	100	100	100
$^{13}C_{12}$-3,4,4',5-TeCB	81L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4'-PeCB	105L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,4,4',5-PeCB	114L	100	100	100	100	100	100
$^{13}C_{12}$-2,3',4,4',5-PeCB	118L	100	100	100	100	100	100
$^{13}C_{12}$-2',3,4,4',5-PeCB	123L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4',5-PeCB	126L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5-HxCB	156L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB	157L	100	100	100	100	100	100
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	167L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	169L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5-HpCB	170L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,4,4',5,5'-HpCB	180L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5,5'-HpCB	189L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB	194L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB	206L	100	100	100	100	100	100
$^{13}C_{12}$-DeCB	209L	100	100	100	100	100	100
Cleanup Standards							
$^{13}C_{12}$-3,4,4',5-TriCB	32L	0.2	1.0	5.0	50	400	--
$^{13}C_{12}$-2,3,3',5,5'-PeCB	111L	0.2	1.0	5.0	50	400	--
Recovery Standards							
$^{13}C_{6}$-4-MoCB	3L6	100	100	100	100	100	100
$^{13}C_{12}$-2,4'-DiCB	8L	100	100	100	100	100	100
$^{13}C_{12}$-3,4,4'-TrCB	37L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',5,5'-TeCB	52L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4',5,5'-PeCB	101L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3',4,4',5'-HxCB	138L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	178L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB	202L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4',5,5',6,6'-NoCB	208L	100	100	100	100	100	100
Labeled Sampling Surrogates							
$^{13}C_{12}$-2,4',5-TriCB	31L	0.2	1.0	5.0	50	400	2000
$^{13}C_{12}$-2,2',3,5',6-PeCB	95L	0.2	1.0	5.0	50	400	2000
$^{13}C_{12}$-2,2',4,4',5,5'-HxCB	153L	0.2	1.0	5.0	50	400	2000

Notes: 1. Suffix "L" indicates labeled compound 2. Section 15.3, calibration verification solution

Table 7

GC Window Defining Mixture

SPB-Octyl

Congener Group	First Eluted		Last Eluted	
Mono	1	2-	3	4-
Di	4	2,2'-	15	4,4'-
Tri	19	2,2',6-	37	3,4,4'-
Tetra	54	2,2',6,6'-	77	3,3',4,4'-
Penta	104	2,2',4,6,6'-	126	3,3',4,4',5-
Hexa	155	2,2',4,4',6,6'-	169	3,3',4,4',5,5'-
Hepta	188	2,2',3,4',5,6,6'-	189	2,3,3',4,4',5,5'-
Octa	202	2,2',3,3',5,5',6,6'-	205	2,3,3',4,4',5,5',6-
Nona	208	2,2',3,3',4,5,5',6,6'-	206	2,2',3,3',4,4',5,5',6-
Deca	209	2,2',3,3',4,4',5,5',6,6'-	209	2,2',3,3',4,4',5,5',6,6'-

SPB-Octyl Resolution Test Compounds

23	2,3,5-trichlorobiphenyl
34	2',3,5-trichlorobiphenyl (2,3',5'-trichlorobiphenyl)
182	2,2',3,4,4',5,6'-heptachlorobiphenyl
187	2,2',3,4',5,5',6-heptachlorobiphenyl

Table 8

Ions Monitored for HRGC/HRMS Analysis of PCBs

Descriptor	Accurate Mass	Ion ID	Elemental Composition	Analyte
1	188.0393	M	$C_{12}H_9{}^{35}Cl$	Mono
	190.0363	M+2	$C_{12}H_9{}^{37}Cl$	Mono
	192.9888	Lock	C_5F_7	PFK
	194.0594	M	$^{12}C_6{}^{13}C_6H_9{}^{35}Cl$	Mono-13C6
	196.0565	M+2	$^{12}C_6{}^{13}C_6H_9{}^{37}Cl$	Mono-13C6
	200.0795	M	$^{13}C_{12}H_9{}^{35}Cl$	Mono-13C12
	202.0766	M+2	$^{13}C_{12}H_9{}^{37}Cl$	Mono-13C12
	222.0003	M	$C_{12}H_8{}^{35}Cl_2$	Di
	223.9974	M+2	$C_{12}H_8{}^{35}Cl^{37}Cl$	Di
	234.0406	M	$^{13}C_{12}H_8{}^{35}Cl_2$	Di-13C
	236.0376	M+2	$^{13}C_{12}H_8{}^{35}Cl^{37}Cl$	Di-13C
	255.9613	M	$C_{12}H_7{}^{35}Cl_3$	Tri
	257.9584	M+2	$C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Tri
	268.0016	M	$^{13}C_{12}H_7{}^{35}Cl_3$	Tri-13C
	268.9824	QC	C_5F_{11}	PFK
	269.9986	M+2	$^{13}C_{12}H_7{}^{35}$[redacted]^{37}Cl	Tri-13C
	289.9224	M	$C_{12}H_6{}^{35}Cl_4$	Tetra
	291.9194	M+2	$C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Tetra
2	255.9613	M	$C_{12}H_7{}^{35}Cl_3$	Tri
	257.9584	M+2	$C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Tri
	268.0016	M	$^{13}C_{12}H_7{}^{35}Cl_3$	Tri-13C
	268.9824	Lock	C_5F_{11}	PFK
	269.9986	M+2	$^{13}C_{12}H_7{}^{35}Cl_2{}^{37}Cl$	Tri-13C
	289.9224	M	$C_{12}H_6{}^{35}Cl_4$	Tetra
	291.9194	M+2	$C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Tetra
	301.9626	M	$^{13}C_{12}H_6{}^{35}Cl_4$	Tetra-13C
	303.9597	M+2	$^{13}C_{12}H_6{}^{35}Cl_3{}^{37}Cl$	Tetra-13C
	325.8804	M+2	$C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Penta
	327.8775	M+4	$C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Penta
	337.9207	M+2	$^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Penta-13C
	339.9178	M+4	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Penta-13C
	342.9792	QC	C_8F_{13}	PFK
	359.8415	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Hexa
	361.8385	M+4	$C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Hexa

Table 8 Continued

Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs

Descriptor	Accurate Mass	Ion ID	Elemental Composition	Analyte
3	325.8804	M+2	$C_{12}H_5{}^{35}Cl_4{}^{37}$[illegible]	Penta
	327.8775	M+4	$C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Penta
	337.9207	M+2	$^{13}C_{12}H_5{}^{35}Cl_4{}^{37}Cl$	Penta-13C
	339.9178	M+4	$^{13}C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$	Penta-13C
	342.9792	Lock	C_8F_{13}	PFK
	359.8415	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Hexa
	361.8385	M+4	$C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Hexa
	371.8817	M+2	$^{13}C_{12}H_4{}^{35}Cl_5{}^{37}Cl$	Hexa-13C
	373.8788	M+4	$^{13}C_{12}H_4{}^{35}Cl_4{}^{37}Cl_2$	Hexa-13C
	393.8025	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Hepta
	395.7995	M+4	$C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Hepta
	405.8428	M+2	$^{13}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Hepta-13C
	407.8398	M+4	$^{13}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Hepta-13C
	427.7635	M+2	$C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Octa
	429.7606	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Octa
	430.9728	QC	C_9F_{17}	PFK
	439.8038	M+2	$^{13}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Octa-13C
	441.8008	M+4	$^{13}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Octa-13C
4	393.8025	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Hepta
	395.7995	M+4	$C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Hepta
	404.9760	Lock	$C_{10}F_{15}$	PFK
	405.8428	M+2	$^{13}C_{12}H_3{}^{35}Cl_6{}^{37}Cl$	Hepta-13C
	407.8398	M+4	$^{13}C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$	Hepta-13C
	427.7635	M+2	$C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Octa
	429.7606	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Octa
	439.8038	M+2	$^{13}C_{12}H_2{}^{35}Cl_7{}^{37}Cl$	Octa-13C
	441.8008	M+4	$^{13}C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2$	Octa-13C
	463.7216	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2$	Nona
	465.7187	M+6	$C_{12}H^{35}Cl_6{}^{37}Cl_3$	Nona
	475.7619	M+4	$^{13}C_{12}H^{35}Cl_7{}^{37}Cl_2$	Nona-13C
	477.7589	M+6	$^{13}C_{12}H^{35}Cl_6{}^{37}Cl_3$	Nona-13C
	497.6826	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2$	Deca
	499.6797	M+6	$C_{12}{}^{35}Cl_7{}^{37}Cl_3$	Deca
	504.9697	QC	$C_{12}F_{19}$	PFK
	509.7229	M+4	$^{13}C_{12}{}^{35}Cl_8{}^{37}Cl_2$	Deca-13C
	511.7199	M+6	$^{13}C_{12}{}^{35}Cl_7{}^{37}Cl_3$	Deca-13C

1. Nuclidic masses used: H = 1.007825 C = 12.00000 ^{13}C = 13.003355 F = 18.9984
O = 15.994915 ^{35}Cl = 34.968853 ^{37}[illegible] = 36.965903

Table 9

Theoretical Ion Abundance Ratios and Their Control Limits for PCBs

Chlorine Atoms	m/z #1	Rel. Abund.[1]	m/z #2	Rel. Abund.[1]	Ratio (mz #1)/(m/z #2)	Control Limits[2] Lower	Control Limits[2] Upper
1	188 (M)	100.00	190 (M+2)	32.81	3.05	2.59	3.51
2	222 (M)	100.00	224 (M+2)	64.79	1.54	1.31	1.77
3	256 (M)	100.00	258 (M+2)	96.74	1.03	0.88	1.19
4	290 (M)	77.68	292 (M+2)	100.00	0.78	0.66	0.89
5	326 (M+2)	100.00	328 (M+4)	64.45	1.55	1.32	1.78
6	360 (M+2)	100.00	362 (M+4)	80.42	1.24	1.06	1.43
7	394 (M+2)	100.00	396 (M+4)	96.40	1.04	0.88	1.19
8	428 (M+2)	88.98	430 (M+4)	100.00	0.89	0.76	1.02
9	464 (M+4)	100.00	464 (M+6)	74.95	1.33	1.13	1.53
10	498 (M+4)	100.00	500 (M+6)	85.61	1.17	0.99	1.34

1 The relative abundance was calculated using the method described in: Pretsch, Clerc, Seibl, Simon, *Tables of Spectral Data for Structure Determination of Organic Compounds*, Second Edition, Springer-Verlag, 1989. The natural isotopic abundances of C, H, and Cl were obtained from "Table of the Isotopes", *Handbook of Chemistry and Physics*, 71st edition, CRC, 1990-1991.

2 QC Limits represent +/- 15 percent window around the theoretical ion abundance ratio.

Table 10

Acceptance Criteria for Performance Tests

PCB congener	IUPAC[1]	Test Conc. (ng/mL)	IPR %RSD	IPR X^2	OPR (LCS)[2]	VER[2]
4-chlorobiphenyl	3	50	40	30-70	25-75	35-65
4,4'-dichlorobiphenyl	15	50	40	30-70	25-75	35-65
3,4,4'-trichlorobiphenyl	37	50	40	30-70	25-75	35-65
3,3',4,4'-tetrachlorobiphenyl	77	50	40	30-70	25-75	35-65
3,4,4',5-tetrachlorobiphenyl	81	50	40	30-70	25-75	35-65
2,3,3',4,4'-pentachlorobiphenyl	105	50	40	30-70	25-75	35-65
2,3,4,4',5-pentachlorobiphenyl	114	50	40	30-70	25-75	35-65
2,3',4,4',5-pentachlorobiphenyl	118	50	40	30-70	25-75	35-65
2',3',4,4',5-pentachlorobiphenyl	123	50	40	30-70	25-75	35-65
3,3',4,4',5-pentachlorobiphenyl	126	50	40	30-70	25-75	35-65
2,3,3',4,4',5-hexachlorobiphenyl	156	50	40	30-70	25-75	35-65
2,3,3',4,4',5'-hexachlorobiphenyl	167	50	40	30-70	25-75	35-65
3,3',4,4',5,5'-hexachlorobiphenyl	169	50	40	30-70	25-75	35-65
2,2',3,3',4,4',5-heptachlorobiphenyl	170	50	40	30-70	25-75	35-65
2,2',3,4,4',5,5'-heptachlorobiphenyl	180	50	40	30-70	25-75	35-65
2,3,3',4,4',5,5'-heptachlorobiphenyl	189	50	40	30-70	25-75	35-65
2,3,3',4,4',5,5',6-octachlorobiphenyl	205	50	40	30-70	25-75	35-65
2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	206	50	40	30-70	25-75	35-65
2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	209	50	40	30-70	25-75	35-65
Labeled Internal Standards						
$^{13}C_{12}$-4-chlorobiphenyl	$3L_{12}$	100	50	35-135	30-140	50-150
$^{13}C_{12}$-4,4'-dichlorobiphenyl	15L	100	50	35-135	30-140	50-150
$^{13}C_{12}$-2,4,4'-trichlorobiphenyl	28L	100	50	35-135	30-140	50-150
$^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl	77L	100	50	35-135	30-140	50-150
$^{13}C_{12}$-3,4,4',5-tetrachlorobiphenyl	81L	100	50	35-135	30-140	50-150
$^{13}C_{12}$-2,3,3',4,4'-pentachlorobiphenyl	105L	100	50	35-135	30-140	50-150
$^{13}C_{12}$2,3,4,4',5-pentachlorobiphenyl -	114L	100	50	35-135	30-140	50-150
$^{13}C_{12}$-2,3',4,4',5-pentachlorobiphenyl	118L	100	50	35-135	30-140	50-150
$^{13}C_{12}$-2',3',4,4',5-pentachlorobiphenyl	123L	100	50	35-135	30-140	50-150
$^{13}C_{12}$-3,3',4,4',5-pentachlorobiphenyl	126L	100	50	35-135	30-140	50-150
$^{13}C_{12}$-2,3,3',4,4',5-hexachlorobiphenyl	156L	100	50	35-135	30-140	50-150
$^{13}C_{12}$-2,3,3',4,4',5'-hexachlorobiphenyl	157L	100	50	35-135	30-140	50-150
$^{13}C_{12}$-2,3',4,4',5,5'-hexachlorobiphenyl	167L	100	50	35-135	30-140	50-150
$^{13}C_{12}$-3,3',4,4',5,5'-hexachlorobiphenyl	169L	100	50	35-135	30-140	50-150
$^{13}C_{12}$-2,2',3,3',4,4',5-heptachlorobiphenyl	170L	100	50	35-135	30-140	50-150
$^{13}C_{12}$-2,2',3,4,4',5,5'-heptachlorobiphenyl	180L	100	50	35-135	30-140	50-150
$^{13}C_{12}$-2,3,3',4,4',5,5'-heptachlorobiphenyl	189L	100	50	35-135	30-140	50-150
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-octachlorobiphenyl	194L	100	50	35-135	30-140	50-150
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	206L	100	50	35-135	30-140	50-150
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	209L	100	50	35-135	30-140	50-150
Cleanup standards						
$^{13}C_{12}$-2,4',6-trichlorobiphenyl	32L	100	45	45-120	40-125	60-130
$^{13}C_{12}$-2,3,3',5,5'-pentachlorobiphenyl	111L	100	45	45-120	40-125	60-130
Labeled Surrogate Standards						
$^{13}C_{12}$-2,4',5-trichlorobiphenyl	31L	50	NA	NA	NA	35-65
$^{13}C_{12}$-2,2',3,5',6-pentachlorobiphenyl	95L	50	NA	NA	NA	35-65
$^{13}C_{12}$-2,2',4,4',5,5'-hexachlorobiphenyl	153L	50	NA	NA	NA	35-65

Notes:
1 Test concentrations are based on ng/mL in the sample extract or standard solution.

Table 11

Retention Times[1] of Isomers on the SPB-Octyl Column for the PCB Standard Mixes

PCB Congener Mix 1 (Accustandard S-4687-A)[2]

Cl Level	BZ No.[4]	RT	Cl Level	BZ No.[4]	RT	Cl Level	BZ No.[4]	RT
1	2	16:11	4	78	37:58	6	161	42:50
2	10	16:55	4	81	38:28	6	153	43:21
2	9	18:59	5	96	30:22	6	130	44:05
2	6	19:29	5	103	32:15	6	129	44:52
2	8	19:59	5	95	33:09	6	166	46:04
2	14	21:45	5	88	33:56	6	159	47:03
2	11	22:46	5	89	34:48	6	167	47:52
3	30	22:19	5	92	35:33	6	156	49:10
3	27	23:10	5	113	36:05	7	179	42:25
3	32	24:05	5	83	36:43	7	176	43:22
3	34	25:21	5	119	37:16	7	178	45:09
3	26	25:51	5	87	37:30	7	175	45:53
3	31	26:32	5	85	38:00	7	183	46:46
3	33	27:06	5	82	38:48	7	177	47:38
3	36	29:09	5	120	39:29	7	171	48:17
3	38	30:12	5	124	40:43	7	172	49:51
3	35	30:46	5	106	41:17	7	191	50:57
4	50	26:11	5	122	41:56	7	170	51:58
4	45	27:01	5	105	42:51	7	190	52:32
4	52	28:48	5	127	44:13	8	200/201	48:33
4	49	29:19	6	152	36:12	8	204	49:13
4	75	30:12	6	136	36:49	8	199/200	49:43
4	41	30:56	6	148	38:32	8	198	52:34
4	72	32:02	6	151	39:13	8	196	53:17
4	57	32:49	6	144	39:51	8	195	54:58
4	63	33:38	6	143	40:35	8	194	57:22
4	66	34:20	6	142	41:19	9	207	55:38
4	79	37:19	6	133	42:03			

PCB Congener Mix 2 (Accustandard S-4687-B)[2]

Cl Level	BZ No.[4]	RT	Cl Level	BZ No.[4]	RT	Cl Level	BZ No.[4]	RT
2	7	19:10	4	55	34:32	6	139	40:49
2	5	19:54	4	60	35:25	6	132	41:41
2	12	23:09	5	94	32:37	6	165	42:25
3	18	22:27	5	100	33:11	6	168	43:24
3	24	23:17	5	91	33:59	6	137	44:17
3	23	25:28	5	121	35:00	6	160	44:56
3	28	26:52	5	90	36:07	6	128	46:13
3	22	27:35	5	99	36:45	6	162	47:22
3	39	29:34	5	109/108	37:16	6	157	49:13
4	53	26:14	5	117	38:00	7	184	42:48
4	51	27:02	5	111	38:56	7	186	43:51
4	73	28:55	5	108/107	40:43	7	187	46:05
4	48	29:37	5	118	41:27	7	185	46:56
4	62	30:14	5	114	42:03	7	181	47:55
4	71	31:02	6	150	36:23	7	192	50:08
4	68	32:21	6	145	37:05	8	197	49:29
4	58	33:08	6	135	39:20	8	201/199	52:35
4	61	33:51	6	149	40:14	8	203	53:29

Table 11 **Continued**

Retention Times[1] of Isomers on the SPB-Octyl Column for the PCB Standard Mixes[2,3]

PCB Congener Mix 3 (Accustandard S-4687-C)[2]

Cl Level	BZ No.[4]	RT	Cl Level	BZ No.[4]	RT	Cl Level	BZ No.[4]	RT
2	13	23:10	4	80	35:36	6	140	40:51
3	17	22:53	5	93	33:18	6	146	42:42
3	29	25:51	5	84	34:22	6	141	43:41
3	20	26:54	5	101	36:12	6	164	44:30
4	46	27:22	5	112	36:54	6	158	45:09
4	65	29:52	5	86	37:25	7	182	46:21
4	59	30:17	5	116	38:06	7	174	47:05
4	40	31:02	5	107/109	40:58	7	173	48:14
4	67	33:16	6	154	39:24	7	193	50:32
4	76	33:58	6	147	40:16			

PCB Congener Mix 4 (Accustandard S-4687-D)[2]

Cl Level	BZ No.[4]	RT	Cl Level	BZ No.[4]	RT	Cl Level	BZ No.[4]	RT
3	25	26:08	4	64	31:17	5	123	41:06
3	21	27:01	4	70	33:58	6	134	40:32
4	69	29:14	5	102	33:26	6	131	41:08
4	47	29:56	5	97	37:25	6	163	44:47
4	42	30:31	5	115	38:22	7	180	50:33

PCB Congener Mix 5 (Accustandard S-4687-E)[2]

Cl Level	BZ No.[4]	RT	Cl Level	BZ No.[4]	RT	Cl Level	BZ No.[4]	RT
1	1	13:46	4	74	34:00	6	169	52:38
1	3	16:23	4	56	35:07	7	188	41:58
2	4	16:47	4	77	39:07	7	189	55:11
2	15	23:33	5	104	29:53	8	202	47:35
3	19	20:23	5	98	33:29	8	205	57:52
3	16	23:28	5	125	37:25	9	208	54:35
3	37	31:18	5	110	38:23	9	206	59:43
4	54	23:55	5	126	46:02	10	209	1:01:22
4	43	29:06	6	155	35:48			
4	44	30:00	6	138	44:47			

Notes:

1 Source - Brian Fowler, Axys Analytical Services Ltd., Fax to David Thal, Quanterra, Inc., November 23, 1998.

2 Accustandard products S-4687-A to S-4687-E have been replaced by Accustandard product M-1668A-1 to M-1668A-5.

3 Each congener mix is analyzed separately to establish the retention times of the PCB isomers in the absence of co-eluting isomers. The elution order listed here is used to assign peak identifications in the separate mixture analysis. The retention time established in the analysis of the separate mixtures is then used to establish peak identifications in the combined 209 isomer standard. (See sections 10.2.3)

4 BZ/IUPAC Number, if different.

Figure 1

Recommended GC Operating Conditions

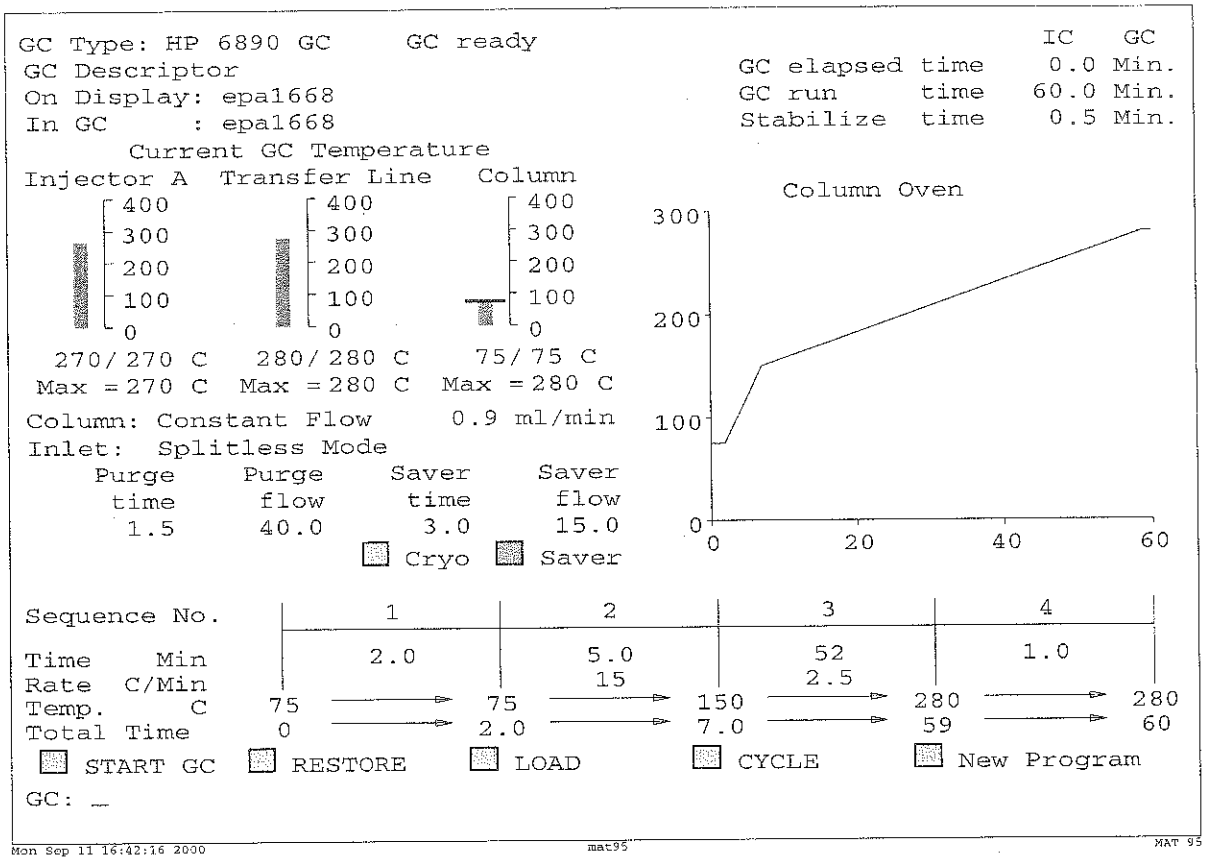
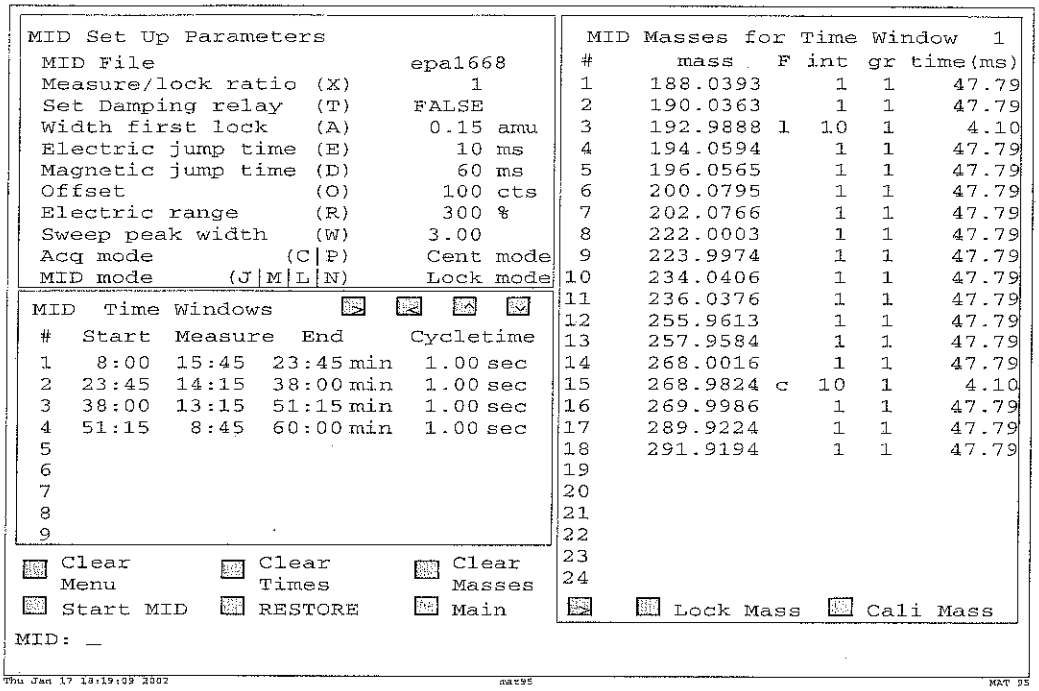


Figure 2

Recommended MID Descriptors



MID Set Up Parameters

MID File		epa1668
Measure/lock ratio	(X)	1
Set Damping relay	(T)	FALSE
Width first lock	(A)	0.15 amu
Electric jump time	(E)	10 ms
Magnetic jump time	(D)	60 ms
Offset	(O)	100 cts
Electric range	(R)	300 %
Sweep peak width	(W)	3.00
Acq mode	(C|P)	Cent mode
MID mode	(J|M|L|N)	Lock mode

MID Time Windows

#	Start	Measure	End	Cycletime
1	8:00	15:45	23:45 min	1.00 sec
2	23:45	14:15	38:00 min	1.00 sec
3	38:00	13:15	51:15 min	1.00 sec
4	51:15	8:45	60:00 min	1.00 sec
5				
6				
7				
8				
9				

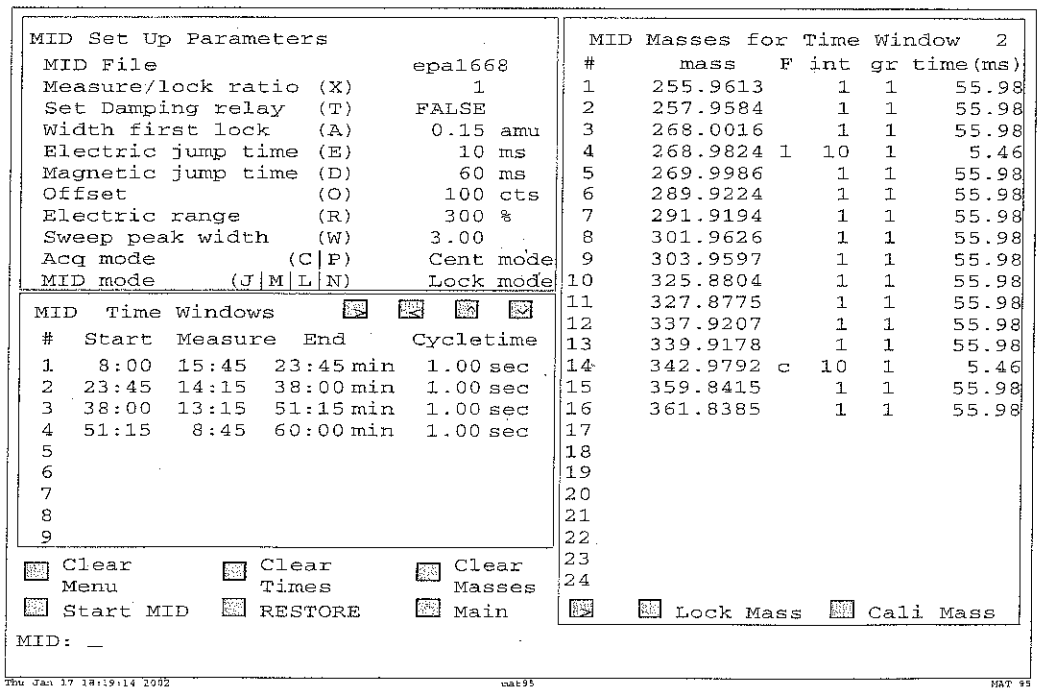
MID Masses for Time Window 1

#	mass	F	int	gr	time(ms)
1	188.0393		1	1	47.79
2	190.0363		1	1	47.79
3	192.9888	l	10	1	4.10
4	194.0594		1	1	47.79
5	196.0565		1	1	47.79
6	200.0795		1	1	47.79
7	202.0766		1	1	47.79
8	222.0003		1	1	47.79
9	223.9974		1	1	47.79
10	234.0406		1	1	47.79
11	236.0376		1	1	47.79
12	255.9613		1	1	47.79
13	257.9584		1	1	47.79
14	268.0016		1	1	47.79
15	268.9824	c	10	1	4.10
16	269.9986		1	1	47.79
17	289.9224		1	1	47.79
18	291.9194		1	1	47.79
19					
20					
21					
22					
23					
24					

Clear Menu | Clear Times | Clear Masses
Start MID | RESTORE | Main
Lock Mass | Cali Mass

MID: _

Thu Jan 17 18:19:09 2002 mat95 MAT 95



MID Set Up Parameters

MID File		epa1668
Measure/lock ratio	(X)	1
Set Damping relay	(T)	FALSE
Width first lock	(A)	0.15 amu
Electric jump time	(E)	10 ms
Magnetic jump time	(D)	60 ms
Offset	(O)	100 cts
Electric range	(R)	300 %
Sweep peak width	(W)	3.00
Acq mode	(C|P)	Cent mode
MID mode	(J|M|L|N)	Lock mode

MID Time Windows

#	Start	Measure	End	Cycletime
1	8:00	15:45	23:45 min	1.00 sec
2	23:45	14:15	38:00 min	1.00 sec
3	38:00	13:15	51:15 min	1.00 sec
4	51:15	8:45	60:00 min	1.00 sec
5				
6				
7				
8				
9				

MID Masses for Time Window 2

#	mass	F	int	gr	time(ms)
1	255.9613		1	1	55.98
2	257.9584		1	1	55.98
3	268.0016		1	1	55.98
4	268.9824	l	10	1	5.46
5	269.9986		1	1	55.98
6	289.9224		1	1	55.98
7	291.9194		1	1	55.98
8	301.9626		1	1	55.98
9	303.9597		1	1	55.98
10	325.8804		1	1	55.98
11	327.8775		1	1	55.98
12	337.9207		1	1	55.98
13	339.9178		1	1	55.98
14	342.9792	c	10	1	5.46
15	359.8415		1	1	55.98
16	361.8385		1	1	55.98
17					
18					
19					
20					
21					
22					
23					
24					

Clear Menu | Clear Times | Clear Masses
Start MID | RESTORE | Main
Lock Mass | Cali Mass

MID: _

Thu Jan 17 18:19:14 2002 mat95 MAT 95

Figure 2 Continued

Recommended MID Descriptors

```
MID Set Up Parameters
 MID File                          epa1668
 Measure/lock ratio  (X)             1
 Set Damping relay   (T)          FALSE
 Width first lock    (A)          0.15 amu
 Electric jump time  (E)            10 ms
 Magnetic jump time  (D)            60 ms
 Offset              (O)           100 cts
 Electric range      (R)           300 %
 Sweep peak width    (W)          3.00
 Acq mode          (C|P)          Cent mode
 MID mode      (J|M|L|N)          Lock mode

MID  Time Windows
 #   Start  Measure  End       Cycletime
 1    8:00  15:45   23:45 min   1.00 sec
 2   23:45  14:15   38:00 min   1.00 sec
 3   38:00  13:15   51:15 min   1.00 sec
 4   51:15   8:45   60:00 min   1.00 sec
 5
 6
 7
 8
 9

 Clear Menu      Clear Times     Clear Masses
 Start MID       RESTORE         Main

MID: _
```

```
MID Masses for Time Window   3
#       mass    F int gr time(ms)
1     325.8804      1  1    47.79
2     327.8775      1  1    47.79
3     337.9207      1  1    47.79
4     339.9178      1  1    47.79
5     342.9792 l   10  1     4.10
6     359.8415      1  1    47.79
7     361.8385      1  1    47.79
8     371.8817      1  1    47.79
9     373.8788      1  1    47.79
10    393.8025      1  1    47.79
11    395.7995      1  1    47.79
12    405.8428      1  1    47.79
13    407.8398      1  1    47.79
14    427.7635      1  1    47.79
15    429.7606      1  1    47.79
16    430.9728 c   10  1     4.10
17    439.8038      1  1    47.79
18    441.8008      1  1    47.79
19
20
21
22
23
24
    Lock Mass    Cali Mass
```

Thu Jan 17 18:19:18 2002 mat95 MAT 95

```
MID Set Up Parameters
 MID File                          epa1668
 Measure/lock ratio  (X)             1
 Set Damping relay   (T)          FALSE
 Width first lock    (A)          0.15 amu
 Electric jump time  (E)            10 ms
 Magnetic jump time  (D)            60 ms
 Offset              (O)           100 cts
 Electric range      (R)           300 %
 Sweep peak width    (W)          3.00
 Acq mode          (C|P)          Cent mode
 MID mode      (J|M|L|N)          Lock mode

MID  Time Windows
 #   Start  Measure  End       Cycletime
 1    8:00  15:45   23:45 min   1.00 sec
 2   23:45  14:15   38:00 min   1.00 sec
 3   38:00  13:15   51:15 min   1.00 sec
 4   51:15   8:45   60:00 min   1.00 sec
 5
 6
 7
 8
 9

 Clear Menu      Clear Times     Clear Masses
 Start MID       RESTORE         Main

MID: _
```

```
MID Masses for Time Window   4
#       mass    F int gr time(ms)
1     393.8025      1  1    47.79
2     395.7995      1  1    47.79
3     404.9760 l   10  1     4.10
4     405.8428      1  1    47.79
5     407.8398      1  1    47.79
6     427.7635      1  1    47.79
7     429.7606      1  1    47.79
8     439.8038      1  1    47.79
9     441.8008      1  1    47.79
10    463.7216      1  1    47.79
11    465.7187      1  1    47.79
12    475.7619      1  1    47.79
13    477.7589      1  1    47.79
14    497.6826      1  1    47.79
15    499.6797      1  1    47.79
16    504.9697 c   10  1     4.10
17    509.7229      1  1    47.79
18    511.7199      1  1    47.79
19
20
21
22
23
24
    Lock Mass    Cali Mass
```

Thu Jan 17 18:15:31 2002 mat95 MAT 95

Figure 3

Example Data Review Checklist

STL Knoxville Specialty Organics Group GC/MS Initial Calibration Data Review / Narrative Checklist
Method or SOP Number: _____

PFK Date/Time:		Inst:		Win Filename:		Col Perf Filename:	

CS1 Filename	CS2 Filename	CS3 Filename	CS4 Filename	CS5 Filename

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Was the mass resolution documented before beginning the initial calibration (HRMS only)?					
2. Was the instrument resolution >10,000 (<100 ppm) on PFK m/z 304.9824 and m/z 380.9760 (at reduced voltage) (HRMS only)?					
3. Was the measured exact mass of m/z 380.9760 (PFK) within 5 ppm at reduced accelerating voltage (HRMS only)?					
4. Was the Window Defining Mixture analyzed and the MID switchpoints set to encompass the retention time windows of each congener group?					
5. Was the Column Performance solution analyzed and the control criteria met?					
6. Were the calibration standard solutions, at the number and concentrations specified in the Method/SOP, analyzed?					
7. Was date/time of analysis verified between analysis header and logbook as correct?					
8. Were the response factors calculated for each labeled standard and unlabeled native analyte using the Method/SOP specified reference compound, quantitation ions, and formula?					
9. Is the %RSD acceptable for all unlabeled native analytes? • Specify QC Limit:_____					
10. Is the %RSD acceptable for all labeled internal standards? • Specify QC Limit:_____					
11. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards?					
12. Are the ion abundance ratios for all labeled and unlabeled analytes within the specified control limits?					
13. If manual integrations were performed, are they clearly identified, initialed and dated?					
14. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
15. Does the ICAL folder contain **complete** data in the following order? Data review checklist, a **complete** runlog, Avg. %RSD summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation (HRMS only), and Total RIC, EICP's and manual integration - for window and all standards, in order from low to high standard.					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

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Figure 3 **Continued**

Example Data Review Checklist

STL Knoxville Specialty Organics Group GC/MS Continuing Calibration Review / Narrative Checklist
Method or SOP Number: _____

Start PFK:		CS3 Filename:		Win Filename:		Inst:	
End PFK:				Col Perf Filename:		ICAL Date:	

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Was the mass resolution documented at both the beginning and end of the 12 hour shift (HRMS only)?					
2. Was the instrument resolution >10,000 (<100 ppm) on PFK m/z 304.9824 and m/z 380.9760 (at reduced voltage) (HRMS only)?					
3. Was the measured exact mass of m/z 380.9760 (PFK) within 5 ppm at reduced accelerating voltage (HRMS only)?					
4. Was date/time of analysis verified between analysis header and logbook as correct?					
5. Was the Window Defining Mixture analyzed and the MID switchpoints set to encompass the retention time windows of each congener group?					
6. Was the Column Performance solution analyzed and the control criteria met?					
7. Was the continuing calibration performed at the beginning of the 12 hour period after successful mass resolution and GC resolution performance check?					
8. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound, quantitation ions, and formula.					
9. Are %D acceptable for all unlabeled native analytes in the calibration? • Specify QC Limit:_____					
10. Are %D acceptable for all labeled standards in the calibration? • Specify QC Limit:_____					
11. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards?					
12. Are the ion abundance ratios for all labeled and unlabeled analytes within the specified control limits?					
13. If manual integrations were performed, are they clearly identified, initialed and dated?					
14. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
15. Does the CCAL folder contain **complete** data in the following order? Data review checklist, a **complete** runlog, CCAL summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation (HRMS only), and Total RIC, EICP's and manual integration - for window and both standards.					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

Figure 3 **Continued**

Example Data Review Checklist

STL Knoxville Specialty Organics Group GC/MS Data Review / Narrative Checklist LOT #_____
Method or SOP Number: _____ **Page 1 of 2**

Batch Number:	

Review Items **A. Initial Calibration**	N/A	Yes	No	Why is data reportible?	2nd Level
1. Was the correct ICAL used for quantitation? (Check 1-2 compounds for batch by manually calculating concentration using the ICAL avg. RF.)					
B. Continuing Calibration					
1. Has a Continuing Calibration Checklist been completed for each analytical batch?					
C. Client Sample AND QC Sample Results					
1. Were all special project requirements met?					
2. Were the header information, prep factors, and dilution factors verified?					
3. Was date/time of analysis verified between analysis header and logbook as correct?					
4. Sample analyses done within preparation and analytical holding time (HT)? *If no, list samples:* _____				HT expired upon receipt. * Client requested analysis after HT expired. Re-extraction done after HT expired. See Comment no. _____.	
5. Are internal standards within QC limits? *If no, list samples and reason (e.g.,* **surl***):* Sample Reason Sample Reason				* **[sup]** Ion suppression due to matrix. * **[low]** Low recovery. S/N >10 and EDL<ML. **[sam]** Not enough sample to re-extract. **[dil]** Dilution showed acceptable %R. **[mtx]** Obvious matrix interference. Further cleanup not possible. * **[unk]** At client's request, data was flagged as estimated and released without further investigation. **[com]** See Comment no. _____.	
6. Were the following qualitative criteria met for all reported analytes: • All analytes within Method/SOP retention time criteria and both ions maximized within ±2 seconds. • The ion abundance ratios for all labeled and unlabeled analytes within the specified control limits. • All peaks ≥2.5 S/N					
7. Were peaks ≥2.5 S/N, which did not meet the above criteria, properly calculated and reported as EMPCs?					
8. Are positive results within calibration range? *If no, list samples:* _____				Sample extracted at lowest possible volume	
11. If manual integrations were performed, are they clearly identified, initialed and dated?					
12. Final report acceptable? (Results correct, DLs calculated correctly, units correct, IS %R correct, appropriate flags used, dilution factor correct, and extraction/ analysis dates correct.)					
13. Was a narrative prepared and all deviations noted?					

* Such action must be taken in consultation with client.

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Figure 3 **Continued**

Example Data Review Checklist

STL Knoxville Specialty Organics Group GC/MS Data Review / Narrative Checklist LOT #_____
Method or SOP Number: _____ **Page 2 of 2**

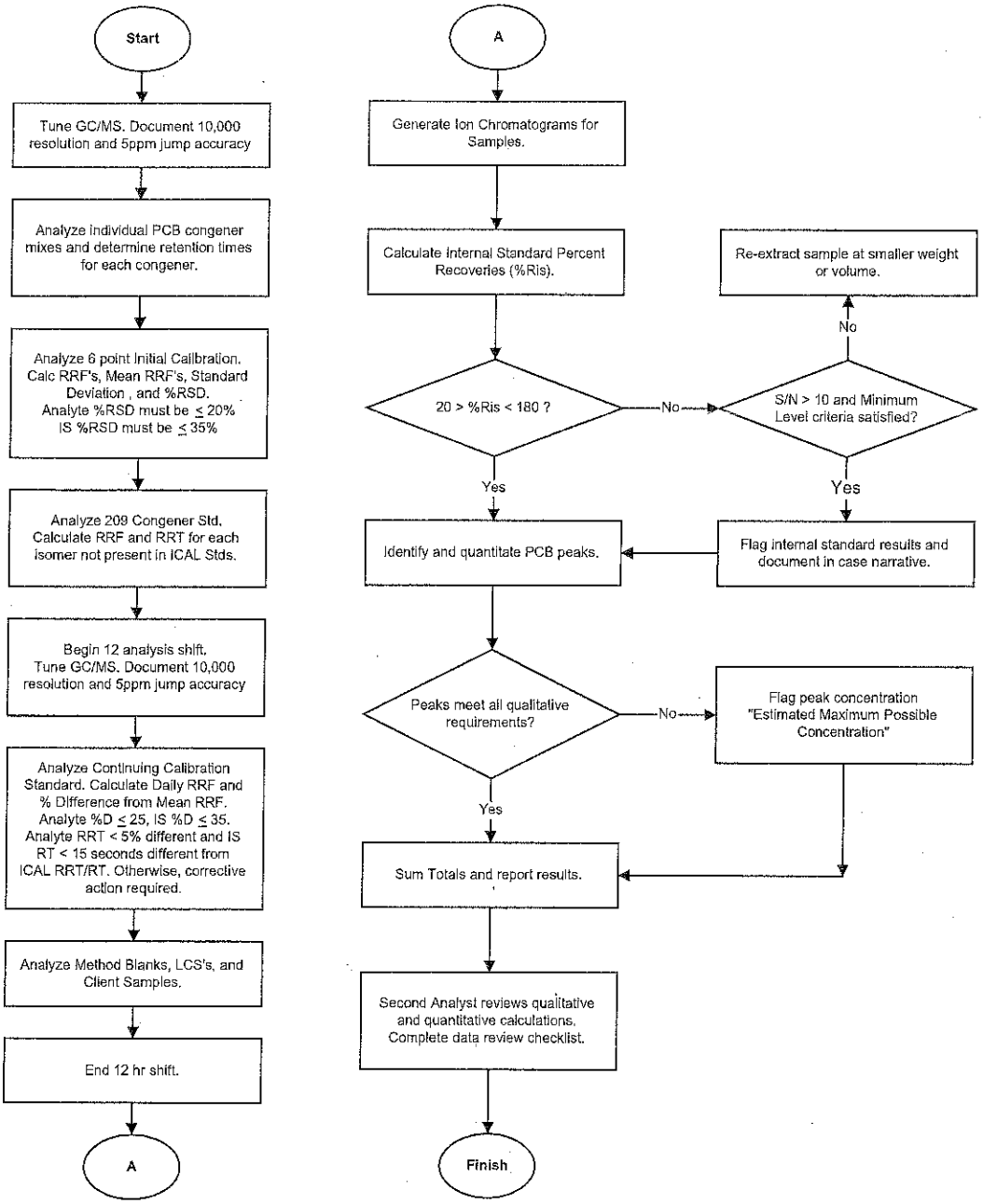
D. Preparation/Matrix QC	N/A	Yes	No	Why is data reportable?	2nd Level
1. LCS done per prep batch and all analytes within laboratory established QC limits? *If no, list LCS ID:* _____				MS/MSD %R and all sample surrogate %R good indicating that problem was confined to the LCS. * Reanalysis not possible-insufficient sample. LCS %R high and affected analyte(s) were <ML in associated samples. See Comment no. _____.	
2. Method blank done per prep batch and method blank or instrument blank analyzed with each sequence?					
3. Method blank internal standard recoveries within QC limits? *If no, list blank ID:* _____				* Internal standards are high and blank demonstrates that analysis is free of contaminants. * Sample internal standards OK and there is no analytes >ML in samples associated with blank.	
4. Are all analytes present in the method blank ≤ ML? *If no, list blank ID:* _____				Sample results are > 20x higher than blank. * There is no analyte > RL in the samples associated with method blank. * Reanalysis not possible-insufficient sample	
4. MS/MSD done per batch and are all recoveries and RPDs within laboratory generated QC limits? *If no, list MS/MSD ID:* _____				LCS showed acceptable results indicating sample matrix effects. LCS showed acceptable results. High native analyte concentration relative to spike level. LCS showed acceptable results. RPD out due to lack of sample homogeneity. See Comment no. _____.	
E. Other					
1. Are all nonconformances documented appropriately and copy included with deliverable?					

Analyst:	Date:	Analyst:	Date:
Comments:		Comments:	

* Such action must be taken in consultation with client.

Figure 4

Analysis Of PCB's by HRGC/HRMS



APPENDIX B
LABORATORY SOP FOR METHOD 8082

STL STANDARD OPERATING PROCEDURE

TITLE: GAS CHROMATOGRAPHIC ANALYSIS BASED ON METHOD 8000B, SW-846 8081A, 8082 8141A, 8151A and 8310

(SUPERSEDES: Revision 5.2)

Prepared by: _____

Reviewed by: _____
Technical Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental, Health and Safety Coordinator

Approved by: _____
Laboratory Director

TABLE OF CONTENTS

List of Tables

1. SCOPE AND APPLICATION

This SOP describes procedures for analysis of organic analytes by Gas Chromatography (GC). The procedures are based on SW-846 methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA). Individual analytes and methods are described in the appendices. Currently, Method SW8021B is not run by STL – Pittsburgh, however other laboratories within STL do run this method.

2. SUMMARY OF METHOD

In general, semivolatile analytes in aqueous samples are prepared for analysis using continuous or separatory funnel liquid / liquid extraction or solid phase extraction (SOP # CORP-OP-0001) Solid samples are prepared using sonication, Soxhlet or pressurized fluid extraction (SOP # CORP-OP-0001).

After the initial preparation step, the sample is introduced to the GC and concentrations of target analytes are measured by the detector response within a defined retention time window, relative to the response to standard concentrations. Internal or external standardization procedures are used as specified in the method appendices.

3. DEFINITIONS

Definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Management Plan (QAMP).

4. INTERFERENCES

Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. In addition, some purge and trap autosamplers are susceptible to port specific contamination. Co-elution of target analytes with non-targets can occur, resulting in false positives or biased high results. In particular, this is a problem with non-selective detectors such as the Flame Ionization Detector (FID). See the appendices for interferences specific to individual tests and suggested corrective actions.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates. The following requirements must be met:

Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded; other gloves will be cleaned immediately. Refer to the STL Chemical Hygiene plan for a complete description of personal protection equipment.

The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. Specific hazards are covered in the appendices.

5.1.1. Opened containers of neat standards will be handled in a fume hood.

5.2. Sample extracts and standards which are in a flammable solvent shall be stored in an explosion-proof refrigerator.

5.3. When using hydrogen gas as a carrier, all precautions listed in the CHP shall be observed.

5.4. Standard preparation and dilution shall be performed inside an operating fume hood.

6. EQUIPMENT AND SUPPLIES

An analytical system complete with a gas chromatograph is required. A data system capable of measuring peak area and/or height is required. Recommended equipment and supplies for individual methods are listed in each method appendix.

7. REAGENTS AND STANDARDS

7.1. Stock Standards

Stock standards are purchased as certified solutions or prepared from pure solutions. Semivolatile stock standard solutions are stored at $\leq 6^{\circ}C$. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before using.

Semivolatile stock standard solutions must be replaced after one year. Stock standards of gases must be replaced at least every week, unless the acceptability of the standard is demonstrated (Less than 20% drift from the initial is an acceptable demonstration). Other volatile stock standards must be replaced every 6 months or sooner, if comparison with check standards prepared from an independent source indicates a problem.

7.1.1. Expiration times for all standards are measured from the time the standard is prepared or from the time that the standard ampoule is opened, if the standard is supplied in a sealed ampoule. If a vendor supplied standard has an earlier expiration date then that date is used.

7.2. Calibration Standards

7.2.1. Congener Calibration Standards

The procedure for preparation of PCB Congener standards is given in Appendix A.

7.2.2. Semivolatile Calibration Standards

Semivolatile calibration standards are prepared as dilutions of the stock standards. Surrogates and internal standards are used as specified in the method appendices. Semivolatile calibration solutions must be refrigerated at $\leq 6^{\circ}C$ and protected from light. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem.

7.3. Gases for carrier and make-up: Hydrogen, Helium, Nitrogen, Argon/Methane.

7.4. Quality control (QC) Standards

QC standards (matrix spiking and LCS standards) are prepared and stored in the same way as calibration standards. They must be made from a stock independent from the calibration standards.

8. SAMPLE PRESERVATION AND STORAGE

Semivolatile extracts must be refrigerated at $\leq 6^{\circ}C$ and analyzed within 40 days of the end of the extraction.

9. QUALITY CONTROL

9.1. Refer to the STL Pittsburgh QC Program document (QA-003) for further details on criteria and corrective actions. Refer to "Project Checklist" for project specific requirements.

9.2. Initial Demonstration of Capability

9.2.1. For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in section 13 must be acceptable before analysis of samples may begin.

9.2.2. For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

9.3. Batch Definition

Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the STL QC Program document (QA-003) for further details of the batch definition.

9.3.1. Quality Control Batch

The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. If insufficient sample is available for an MS/MSD a LCSD may be substituted.

9.4. Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be verified at least annually. The recovery limits are mean recovery +/- 3 standard deviations, unless that limit is tighter than the calibration criteria, in which case limits may be widened. Refer to policy QA-003 for more details.

9.4.1. These limits do not apply to dilutions (except for tests without a separate extraction), but surrogate and matrix spike recoveries will be reported unless the dilution is more than 5X.

9.4.2. All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.4.3. Refer to the QC Program document (QA-003) for further details of control limits.

9.5. Surrogates

All methods must use surrogates to the extent possible. Surrogate recoveries in samples and QC samples must be assessed to ensure that recoveries are within established limits. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze the extract if either of the above checks reveal a problem.

- Reprepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem. Repreparation is not necessary is there is obvious chromatographic interference.
- The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare / reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.5.1. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in-control result is reported.

9.5.2. If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then repreparation or flagging of the data is required.

9.5.3. Refer to the STL QC Program document (QA-003) for further details of the corrective actions.

9.6. Method Blanks

9.6.1. For each batch of samples, analyze a method blank. The method blank consists of reagent water for aqueous semivolatiles samples, and sodium sulfate for semivolatiles soils tests (Refer to SOP No. CORP-OP-0001 for details).

9.6.2. Surrogates are added and the method blank is carried through the entire analytical procedure. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in the associated samples, whichever is higher. Wherever blank contamination is greater than 1/10 the concentrations found in the samples and/or 1/10 of the regulatory limit it is potentially at a level of concern and should be handled as a non-conformance. Blank contamination should always be assessed against project specific requirements (See associated project checklist).

9.6.3. If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone, phthalate esters) the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit. Such action must be taken in consultation with the client.

9.6.4. Re-extraction and reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

9.6.5. If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.7. Instrument Blanks

9.7.1. An instrument blank must be analyzed during any 12 hour period of analysis that does not contain a method blank.

9.7.2. An instrument blank consists of the appropriate solvent with internal standards added. If internal standards are not used the surrogates should be added.

9.7.3. Control criteria are the same as for the method blank, except that only reanalysis of affected samples would be required, not re-extraction.

9.8. Laboratory Control Samples (LCS)

For each batch of samples, analyze a LCS. The LCS contains a representative subset of the analytes of interest, and must contain the same analytes as the matrix spike. The LCS may also contain the full set of analytes. If any analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be repreparation and reanalysis of the batch; however, if the matrix spike and matrix spike duplicate are within limits, the batch may be acceptable.

9.8.1. Refer to the STL QC Program document (QA-003) for further details of the corrective action.

9.8.2. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in control result is reported.

9.8.3. LCS compound lists are included in the appendices.

9.8.4. If full analyte spike lists are used at client request, it will be necessary to allow a percentage of the components to be outside control limits as this would be expected statistically. These requirements should be negotiated with the client.

9.9. Matrix Spikes

- For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in the appendices. Compare the percent recovery and relative percent difference (RPD) to those in the laboratory specific historically generated limits.
- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed.
- If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.
- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed.
- The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, unless the matrix spike components would then be above the calibration range.

9.9.1. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in control result is reported.

9.10. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.11. STL QC Program

Further details of QC and corrective action guidelines are presented in the STL QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

Internal or external calibration may be used. Internal calibration is recommended unless the sample matrix is likely to interfere with the quantitation of the internal standard. In either event prepare standards containing each analyte of interest at a minimum of five concentration levels. The low level standard should be at or below the reporting limit. The other standards define the working range of the detector. Recommended calibration levels are given in the appendices.

10.1. A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns, changing PID lamps or FID jets or replacing the ECD detector. A new calibration is not required after clipping the column, replacing the septum or syringe, or other minor maintenance.

10.2. With the exception of 10.3 below, it is NOT acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or lowest on the curve AND the reporting limit and/or linear range is adjusted accordingly. In any event, at least 5 points must be included in the calibration curve. Quadratic (second order) calibrations require at least six points. Third order calibrations require at least seven points.

10.3. A level may be removed from the calibration if the reason can be clearly documented, for example a broken vial or no purge run. A minimum of five levels must remain in the calibration. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be reanalyzed and the reanalysis used for the calibration. All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours.

10.4. External standard calibration

Quantitation by the external standard method assumes a proportional relationship between the calibration run and the analyte in the sample. To use this approach, introduce each calibration standard into the GC using the technique that will be used for samples. The ratio of the peak height or area response to the mass or concentration injected may be used to prepare a calibration curve.

$$Calibration\ Factor\ (CF) = \frac{Area\ or\ Height\ of\ Peak}{Mass\ Injected\ (ng)}$$

Some data systems may use the inverse of this formula. This is acceptable so long as the same formula is used for standards and samples. It is also possible to use the concentration of the standard rather than the mass injected. (This would require changes in the equations used to calculate the sample concentrations). Use of peak area or height must be consistent. However, if matrix interferences would make quantitation using peak area inaccurate for a particular sample, then peak height may be used as a substitute.

10.5. Internal standard calibration

10.5.1. The internal standard approach assumes that variations in instrument sensitivity, amount injected etc. can be corrected by determining the ratio of the response of the analyte to the response of an internal standard that has been added to the extract. To use this approach, select one or more internal standard(s) that are similar in analytical behavior to the compounds of interest. Recommended internal standards are given in the appendices. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. If the sample matrix interferes with quantitation of the internal standard, then the external standard approach must be used instead. In this event use the response factors from the previous continuing

calibration to quantitate the analytes in the sample with the interference (applies only to the sample with the interference).

10.5.2. Introduce each calibration standard into the GC using the technique that will be used for samples. Response factors (RF) for each compound are calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

Where:

A_s = Response for the analyte to be measured
A_{is} = Response for the internal standard
C_{is} = Concentration of internal standard
C_s = Concentration of the analyte to be determined in the standard

10.6. Calibration curve fits

Average response factor, linear regression, or quadratic curves may be used to fit the data. Average response factor may be used if the average % RSD of the response factors or calibration factors of all the analytes in the calibration standard taken together is $\leq 20\%$. The average %RSD is calculated by summing the RSD value for each analyte and dividing by the total number of analytes.

10.6.1. In general, for environmental analysis, average response factors are the most appropriate calibration model. Linear or curved regression fits should only be used if the analyst has reason to believe that the average RF model does not fit the normal concentration/response behavior of the detector.

10.6.2. Average response factor

The average response factor may be used if the average percent relative standard deviation (%RSD) of all the response factors taken together is $\leq 20\%$.

The equation for average response factor is:

$$\textit{Average response factor} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

Where: n = Number of calibration levels

$\sum_{i=1}^{n} RF_i$ = Sum of response factors for each calibration level

10.6.3. Linear regression

The linear fit uses the following functions:

10.6.3.1. External Standard

$$y = ax + b$$

or

$$x = \frac{(y - b)}{a}$$

Where: y = Instrument response
x = Concentration
a = Slope
b = Intercept

10.6.3.2. Internal Standard

$$C_s = \frac{\left[\frac{A_s C_{is}}{A_{is}} - b\right]}{a}$$

Where: C_s = Concentration in the sample
A_s = Area of target peak in the sample
A_{is} = Area of internal standard in the sample
C_{is} = Concentration of the internal standard

10.6.4. Quadratic curve

The quadratic curve uses the following functions:

10.6.4.1. External standard

$$y = ax + cx^2 + b$$

Where c is the curvature

10.6.4.2. Internal Standard

$$y = a\left(\frac{A_s \times C_{is}}{A_{is}}\right) + c\left(\frac{A_s \times C_{is}}{A_{is}}\right)^2 + b$$

10.7. Evaluation of calibration curves

10.7.1. The percent relative standard error (%RSE) from the calibration curve is used to evaluate the initial calibration. This provides a measure of how much error is associated with using the calibration curve for quantitation.

10.7.2. The least squares regression line is calculated and used to calculate the predicted concentration for each level. The percent relative standard error is calculated as follows:

$$\%\ RSE = 100\% \times \sqrt{\frac{\sum_{i=1}^{N}\left[\frac{C_i - PC_i}{C_i}\right]^2}{(N-P)}}$$

Where:
N = Number of points in the curve
P = Number of parameters in the curve (= 1 for average response factor, 2 for linear, 3 for quadratic)
C_i = True concentration for level i
PC_i = Predicted concentration for level i

Note that when average response factors are used, %RSE is equivalent to %RSD.

10.8. The following requirements must be met for any calibration to be used:

- Response must increase with increasing concentration.
- If a curve is used, the intercept of the curve at zero response must be less than $\pm$ the reporting limit for the analyte.
- The average Relative Standard Error (RSD for average response factors) of the calibration points from the curve used must be $\leq 20\%$.
- Some data systems will not measure the %RSE from a linear or quadratic fit. For the linear case, the correlation coefficient may be used as an alternative to the %RSE, and must be greater than or equal to 0.990. For the quadratic case the Coefficient of Determination may be used, and must be greater or equal to 0.990.

Note: The Relative Standard Error (RSE) is superior to the Correlation Coefficient (r) and Coefficient of Determination (r^2) for testing the fit of a set of calibration points to a line. The lower points on a curve have little effect on r. As a result a curve may have a very good correlation coefficient (>0.995), while also having > 100% error at the low point.

10.9. Weighting of data points

10.9.1. In linear and quadratic calibration fits, the points at the lower end of the calibration curve have less absolute variance than points at the high concentration end of the curve. This can cause severe errors in quantitation at the low end of the calibration. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.10. Non-standard analytes are sometimes requested. For these analytes, it may be acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five point initial calibration. This action must be with client approval. If the analyte is detected in any of the samples, a five point initial calibration must be generated and the sample(s) reanalyzed for quantitation.

10.11. Calibration Verification

10.11.1. 12 hour Calibration

The working calibration curve or RF must be verified by the analysis of a mid point calibration standard at the beginning, after every 12 hours, and at the end of the analysis sequence. The center of each retention time window is updated with each 12 hour calibration. The CCV is varied periodically to check for linearity, this occurs when MDL's are performed.

10.11.2. Calibration Verification

It may be appropriate to analyze a mid point standard more frequently than every 12 hours. If these calibration verification standards are analyzed, requirements are the same as the 12 hour calibration with the exception that retention times are not updated.

10.11.3. Any individual compounds with $\%D \leq 15\%$ meet the calibration criteria. The calibration verification is also acceptable if the average of the %D for all the analytes is $\leq 15\%$. This average is calculated by summing all the absolute %D results in the calibration (including surrogates) and dividing by the number of analytes.

10.11.4. It is not necessary to run a calibration verification standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.

10.11.5. Samples quantitated by external standard methods must be bracketed by calibration verification standards that meet the criteria listed above. Bracketing is not necessary for internal standard methods.

10.11.6. If the analyst notes that a CCV has failed and can document the reason for failure (e.g. no purge, broken vial, carryover from the previous sample etc.) then a second CCV may be analyzed without any adjustments to the instrument. If this CCV meets criteria then the preceding samples have been successfully bracketed. If adjustments to the instrument are performed before the repeat CCV then the preceding samples have not been successfully bracketed but analysis may continue.

10.11.7. In general, it is not advisable to analyze repeat CCVs on unattended runs. If repeat CCVs are analyzed then the first will serve as the bracketing standard for the preceding samples and the last will serve as the CCV for the following samples.

10.11.8. A mult-level calibration verification should be done periodically to verify stability of the intrument over the calibration range. This will be done at a minimum on an annual basis along with the MDLs.

10.11.9. If highly contaminated samples are expected it is acceptable to analyze blanks or primers at any point in the run.

10.11.10. % Difference calculation

% Difference for internal and external methods is calculated as follows

Internal Standard:

$$\%D = \frac{RF_c - \overline{RF}}{\overline{RF}} \times 100$$

External standard:

$$\%D = \frac{CF_c - \overline{CF}}{\overline{CF}} \times 100$$

Where RF_c and CF_c are the response and calibration factors from the continuing calibration

$\overline{RF}$ and $\overline{CF}$ are the average response and calibration factors from the initial calibration

10.11.11. % Drift calculation

% Drift is used for comparing the continuing calibration to a linear or quadratic curve. The criteria for % drift are the same as for % difference

$$\%\ Drift = \frac{Calculated\ Conc. - Theoretical\ Conc.}{Theoretical\ Conc.} \times 100\%$$

10.11.12. Corrective Actions for Continuing Calibration

If the overall average %D of all analytes is greater than $\pm$ 15% corrective action must be taken. This may include clipping the column, changing the liner or other minor instrument adjustments, followed by reanalyzing the standard. If the overall average %D still varies by more than $\pm$ 15%, a new calibration curve must be prepared.

10.11.13. Corrective Action for Samples

For internal standard methods, any samples injected after a standard not meeting the calibration criteria must be reinjected.

For external standard methods, any samples injected after the last good continuing calibration standard must be reinjected.

If the average %D for all the analytes in the calibration is over 15%, but all of the analytes requested for a particular sample have %D $\leq$ 15%, then the analysis is acceptable for that sample.

10.11.14. Each initial calibration will be verified with the analysis of a second source standard. These must be from lots independent of the sources used for the primary calibration standard. This second source standard must at a minimum pass CCV criteria for the compounds being reported from the curve.

11. PROCEDURE

11.1. Extraction

Extraction procedures are referenced in the appendices.

11.2. Cleanup

Cleanup procedures are referenced in the appendices.

11.3. Gas Chromatography

Chromatographic conditions for individual methods are presented in the appendices.

11.4. Sample Introduction

Semivolatile analytes are introduced by direct injection of the extract. Samples, standards, and QC must be introduced using the same procedure.

11.5. Analytical Sequence

An analytical sequence starts with an initial calibration or a daily calibration. Refer to the individual method appendices for method specific details of daily calibrations and analytical sequences.

11.5.1. The daily calibration includes analysis of standards containing all single response analytes and updating the retention time windows.

11.5.2. If there is a break in the analytical sequence of greater than 12 hours, a new analytical sequence must be started with a daily calibration.

11.6. Retention Time Windows

11.6.1. Retention time windows must be specified for all analytes. *A Fixed retention time windows (± .05 minutes) will be used for all GC methods. Alternatively, if it is determined through calculation that wider limits are necessary, the limits will be developed as follows:* Make an injection of all analytes of interest each day over a three day period. Calculate the standard deviation of the three retention times for each analyte (relative retention times may also be used). For multiresponse analytes (e.g., Aroclors) use the retention time of major peaks. Plus or minus three times the standard deviation of the retention times of each analyte defines the retention time window.

11.6.2. The center of the retention time window is the retention time from the last of the three standards. The centers of the windows are updated with the mid point of the initial calibration and each 12 hour calibration. The widths of the windows will remain the same until new windows are generated following the installation of a new column.

11.6.3. *Where calculated limits are being used, if* the retention time window as calculated above is less than +/- 0.05 minutes, use +/- 0.05 minutes as the retention time window. This allows for slight variations in retention times caused by sample matrix.

11.6.4. *Where calculated limits are being used, t*he laboratory must calculate new retention time windows each time a new column is installed. The new windows must be generated within one week of the installation of the new column. Until these standards have been run on the new column, the retention time windows from the old column may be used, updated with the retention times from the new initial calibration.

11.6.5. Corrective Action for Retention Times

The retention times of all compounds in each continuing calibration must be within the retention time windows established by the 12 hour calibration. If this condition is not met, all samples analyzed after the last compliant standard must be reanalyzed unless the following conditions are met for any compound that elutes outside the retention time window:

The retention time of that compound in the standard must be within a retention time range equal to twice the original window.

No peak that would be reportable may be present on the sample chromatogram within an elution time range equal to three times the original retention time window.

11.7. Daily Retention Time Windows

The center of the retention time windows determined in section 11.6 are adjusted to the retention time of each analyte as determined in the 12 hour calibration standards. (See the method 8081A and 8082 appendices for exceptions for multi-response components.) The retention time windows must be updated at the beginning of each analytical sequence and with each 12 hour calibration, but not for any other calibration verification standards.

11.8. Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to SOP CORP-OP-0001 for determination of percent moisture.

11.9. Procedural Variations

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and approved by a supervisor and QA/QC manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. The nonconformance is also addressed in the case narrative. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Qualitative Identification

12.1.1. Tentative identification occurs when a peak is found within the retention time window for an analyte, at a concentration above the reporting limit, or above the MDL if J flags are required. Normally confirmation is required on a second column, but if the detector is sufficiently specific or if the sample matrix is well enough defined, single column analysis may be adequate. In some cases GC/MS confirmation may be required. Client specific requirements may also define the need for second column confirmation and / or GC/MS confirmation. Refer to the appendices for test specific requirements for confirmation. Identification is confirmed if a peak is also present in the retention time window for that analyte on the confirmatory column, at a concentration greater than the reporting limit (MDL if J flag confirmation required).

12.1.2. Dual column quantitation

- For confirmed results, two approaches are available to the analyst;

A) The primary column approach
Or
B) The better result approach

Both are acceptable to avoid the reporting of erroneous or unconfirmed data. The approach used is based on the project requirements.

12.1.2.1. Primary column approach (may be used where indicated as a project requirement)

The result from the primary column is normally reported. The result from the secondary column is reported if any of the following three bulleted possibilities are true.

- There is obvious chromatographic interference on the primary column
- The result on the primary column is > 40% greater than the result on the secondary column
- Continuing or bracketing standard fails on the primary column but is acceptable on the secondary column. (If the primary column result is > 40% higher than the secondary and the primary column calibration fails, then the sample must be evaluated for reanalysis.)

12.1.2.2. Better result approach (default practice of laboratory subject to project requirements)

The lower of the two results is normally reported. The lower result is considered better because the higher result is generally higher because of chromatographic interference. The higher result is reported if any of the following two bulleted possibilities are true.

- There is obvious chromatographic interference on the column with the lower result
- The continuing or bracketing calibration on the column with the lower result fails. (If the higher result is > 40% higher and the calibration on the column with the lower result fails, then the sample must be evaluated for reanalysis.)
- This rule may be reversed to favor reporting of the higher value or the higher value where the results differ by 40% when indicated as a project requirement by the PM.

12.1.3. If the Relative percent difference (RPD) between the response on the two columns is greater than 40%, or if the opinion of an experienced analyst is that the complexity of the matrix is resulting in false positives, the confirmation is suspect and the results are qualified. RPD is calculated using the following formula:

$$RPD = \frac{R_1 - R_2}{\frac{1}{2}(R_1 + R_2)} x100$$

Where R=Result

12.1.4. Multi-response Analytes

For multi-response analytes, the analyst should use the retention time window, but should rely primarily on pattern recognition. The pattern of peaks will normally serve as confirmation.

12.1.5. The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times.

12.1.6 The Lab reports the lower of the two values. If requested by the client, the higher of the two values will be reported.

12.2. Calibration Range

If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. It may be necessary to dilute samples due to matrix.

12.3. Dilutions

Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

12.3.1. Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and only minor matrix peaks are, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgement is required to determine the most concentrated dilution that will not result in instrument contamination.

12.3.2. Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12.4. Interferences

If peak detection is prevented by interferences, further cleanup should be attempted. If no further cleanup is reasonable, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.5. Internal Standard Criteria for Continuing Calibration

If internal standard calibration is used, then the internal standard response in a continuing calibration standard must be within 50 to 150% of the response in the mid level of the initial calibration.

12.6. Calculations

Capabilities of individual data systems may require the use of different formulas than those presented here. When this is the case, the calculations used must be shown to be equivalent and must be documented in an appendix attached to this document.

12.6.1. External Standard Calculations

12.6.1.1. Aqueous samples

$$Concentration\ (mg/L) = \frac{(A_x \times V_t \times D_f)}{(CF \times V_i \times V_s)}$$

Where:

A_x = Response for the analyte in the sample
V_i = Volume of extract injected, µL
D_f = Dilution factor
V_t = Volume of total extract, µL
V_s = Volume of sample extracted or purged, mL
CF = Calibration factor, area or height/ng, Section 10.1

12.6.1.2. Non-aqueous Samples

$$Concentration\ (mg/kg) = \frac{(A_x \times V_t \times D_f)}{(CF \times V_i \times W \times D)}$$

Where:

W = Weight of sample extracted or purged, g

$$D = \frac{100 - \%\ Moisture}{100}$$ (D = 1 if wet weight is required)

12.6.2. Internal Standard Calculations

12.6.2.1. Aqueous Samples

$$Concentration\ (mg/L) = \frac{(A_x \times C_{is} \times D_f)}{(A_{is} \times RF \times V_s)}$$

Where:

C_{is} = Amount of internal standard added, ng
A_{is} = Response of the internal standard
RF = Response factor for analyte

12.6.2.2. Non-aqueous Samples

$$Concentration\ (mg/kg) = \frac{(A_x \times C_{is} \times D_f)}{(A_{is} \times RF \times W \times D)}$$

12.6.3. Surrogate Recovery

Concentrations of surrogate compounds are calculated using the same equations as for the target compounds. The response factor from the initial calibration is used. Surrogate recovery is calculated using the following equation:

$$\%\ \text{Recovery} = \frac{Concentration\ (or\ amount)\ found}{Concentration\ (or\ amount)\ spiked} \times 100$$

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the

method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005.

13.2. Initial Demonstration

Each laboratory must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soils and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid level calibration.

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in each appendix.

13.2.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.2.4. The CCV will be varied perodically to demonstrate verification of linearity of the curve.

13.3. Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, Section 8000B

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the Method Detection Limit. This SOP states that the Method Blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed to be up to 5 times the reporting limit in the blank following consultation with the client.

17.2. Modifications from Previous Revision

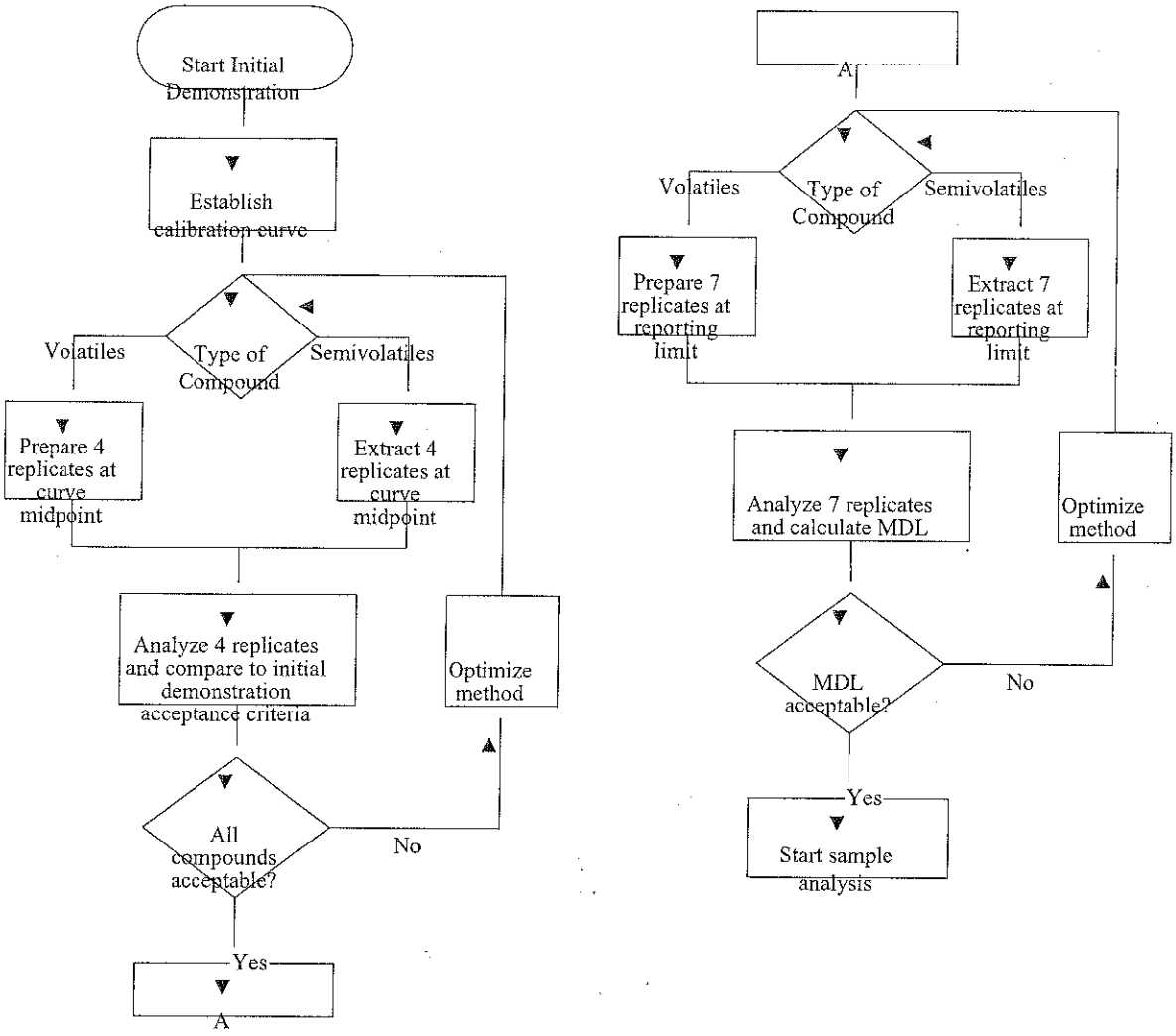
The calibration criteria in section 10.11 have been rewritten to improve consistency with SW-846 and to improve clarity.

17.3. Facility Specific SOPs

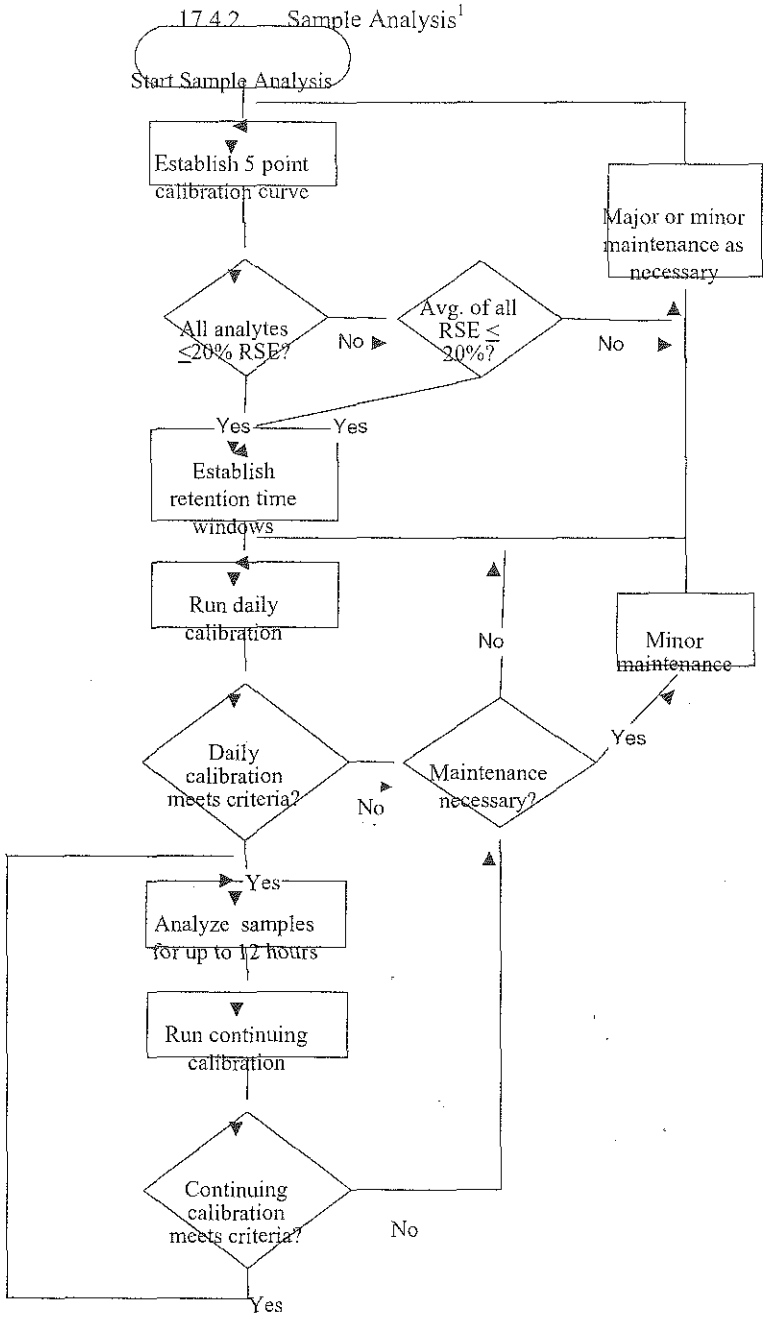
Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.4. Flow Diagrams

17.4.1. Initial demonstration and MDL[1]



[1] This flow diagram is for guidance and cannot cover all eventualities. Consult the SOP text and a supervisor if in doubt.



[1] This flow diagram is for guidance and cannot cover all eventualities. Consult the SOP text and a supervisor if in doubt.

1. SCOPE AND APPLICATION

1.1. This SOP Appendix describes procedures to be used when SW-846 Method 8000B is applied to the analysis of polychlorinated biphenyls (PCB) by GC/ECD. This Appendix is to be applied when SW-846 Method 8082 is requested, and is applicable to extracts derived from any matrix which are prepared according to the appropriate STL sample extraction SOPs. (CORP-OP-0001). The PCBs are determined and quantitated as individual PCB congeners.

Table A-1 lists compounds which are routinely determined by this method and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of PCBs. The PCBs are injected onto the column and separated and detected by electron capture detection. Quantitation is by the external standard method.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for information regarding chromatographic interferences.

4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3. Sulfur will interfere and can be removed using procedures described in SOP CORP-OP-0001.

4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), and Sulfur cleanup (Method 3660). These cleanup procedures are included in SOP # CORP-OP-0001.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2. Congeners have been classified as a potential carcinogen under OSHA. Concentrated solutions of Congeners must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.3. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.

5.4. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Director, EH&S shall be immediately notified and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A ^{63}Ni electron capture detector is required.

6.2. Refer to Table A-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies. All standards for this method must be replaced

7.2. Refer to Table A-3 for details of calibration standards.

7.3. Surrogate Standards

Tetrachloro-m-xylene and BZ-165 are the surrogate standards. Refer to Table A-4 for details of surrogate standards.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Initial Calibration

10.2.1. Refer to Table A-5 for the initial calibration analytical sequence.

10.2.2. The response for each Congener will be calculated by the procedures described in the general method for GC analysis, with the following modifications.

10.2.3. A five point calibration of the individual congeners mix is generated. At least 2 5-points are generated for the congeners to ensure that there is complete resolution of all compounds in the mixes.

10.3. 12 hour Calibration

The 12 hour calibration verification must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration.

10.3.1. The retention time windows for any analytes included in the daily calibration are updated.

10.3.2. For this method samples must be bracketed with successful calibration verification runs.

10.4. Calibration verification

A mid-level calibration mix is analyzed as the calibration verification standard. This is analyzed after every 20 samples or 12 hours, including matrix spikes, LCS, and method blanks. (Depending on the type of samples, it may be advisable to analyze verifications more frequently in order to minimize reruns.).

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP No. CORP-OP-0001.

11.3. Cleanup

Cleanup procedures are described in SOP No. CORP-OP-0001.

11.4. Suggested gas chromatographic conditions are given in Table C-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table A-5.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Identification of Congeners

Retention time windows are used for identification of congeners. Second column confirmation must be performed.

12.2. Surrogate recovery results are calculated and reported for TCMX and BZ-165. Corrective action is only necessary if BZ-165 and TCMX are both outside of acceptance limits.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the main body of this SOP are recovery of 70-130%. The spiking level should be equivalent to a mid level calibration.

13.2. Method detection limits (MDL) are determined for all congeners.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

SW846, Update III, December 1996, Method 8082

17. MISCELLANEOUS

No changes made to this Appendix

17.1. Tables

Table A-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, ng/L or µg/kg			
	water	Low level soil	High level soil	Waste
BZ-1	10.	1.7	8.50	51.0
BZ-3	10.	1.7	8.50	51.0
BZ-5	1.0	0.17	0.85	5.1
BZ-8	1.0	0.17	0.85	5.1
BZ-15	10.	1.7	8.50	51.0
BZ-18	1.0	0.17	0.85	5.1
BZ-28	1.0	0.17	0.85	5.1
BZ-31	1.0	0.17	0.85	5.1
BZ-37	1.0	0.17	0.85	5.1
BZ-44	1.0	0.17	0.85	5.1
BZ-49	1.0	0.17	0.85	5.1
BZ-52	1.0	0.17	0.85	5.1
BZ-66	1.0	0.17	0.85	5.1
BZ-70	1.0	0.17	0.85	5.1
BZ-74	1.0	0.17	0.85	5.1
BZ-77	1.0	0.17	0.85	5.1
BZ-81	1.0	0.17	0.85	5.1
BZ-87	1.0	0.17	0.85	5.1
BZ-90	1.0	0.17	0.85	5.1
BZ-99	1.0	0.17	0.85	5.1
BZ-101	1.0	0.17	0.85	5.1
BZ-105	1.0	0.17	0.85	5.1
BZ-110	1.0	0.17	0.85	5.1
BZ-114	1.0	0.17	0.85	5.1
BZ-115	1.0	0.17	0.85	5.1
BZ-118	1.0	0.17	0.85	5.1
BZ-119	1.0	0.17	0.85	5.1
BZ-123	1.0	0.17	0.85	5.1
BZ-126	1.0	0.17	0.85	5.1
BZ-128	1.0	0.17	0.85	5.1
BZ-138	1.0	0.17	0.85	5.1
BZ-141	1.0	0.17	0.85	5.1
BZ-149	1.0	0.17	0.85	5.1
BZ-151	1.0	0.17	0.85	5.1
BZ-153	1.0	0.17	0.85	5.1
BZ-156	1.0	0.17	0.85	5.1
BZ-157	1.0	0.17	0.85	5.1
BZ-158	1.0	0.17	0.85	5.1
BZ-167	1.0	0.17	0.85	5.1
BZ-168	1.0	0.17	0.85	5.1

Table A-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, ng/L or µg/kg			
	water	Low level soil	High level soil	Waste
BZ-169	1.0	0.17	0.85	5.1
BZ-170	1.0	0.17	0.85	5.1
BZ-177	1.0	0.17	0.85	5.1
BZ-180	1.0	0.17	0.85	5.1
BZ-183	1.0	0.17	0.85	5.1
BZ-184	1.0	0.17	0.85	5.1
BZ-187	1.0	0.17	0.85	5.1
BZ-189	1.0	0.17	0.85	5.1
BZ-194	1.0	0.17	0.85	5.1
BZ-195	1.0	0.17	0.85	5.1
BZ-201	1.0	0.17	0.85	5.1
BZ-202	1.0	0.17	0.85	5.1
BZ-206	1.0	0.17	0.85	5.1
BZ-207	1.0	0.17	0.85	5.1
BZ-209	1.0	0.17	0.85	5.1

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.	Dilution Factor
Ground water	1000 mL	2 mL	1
Low-level Soil	30 g	10 mL	1
High-level soil	30 g	10 mL	5
Waste	1 g	10mL	1

Table C-2

Parameter	Recommended Conditions
Injection port temp	220°C
Detector temp	310
Temperature program	100C for 1.0min, 4°C/min to 292
Column 1	RTx-CLP.32mm id, 0.5µm
Column 2	RTx-CLP2 .32 mm id, 0.25µm
Injection	1-2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen

Table A-3 Calibration Levels ug/mL					
	Level 1	Level 2	Level 3	Level 4	Level 5
BZ-1	0.005	0.01	0.025	0.050	0.10
BZ-3	0.005	0.01	0.025	0.050	0.10
BZ-5	0.0005	0.001	0.0025	0.0050	0.010
BZ-8	0.0005	0.001	0.0025	0.0050	0.010
BZ-15	0.005	0.01	0.025	0.050	0.10
BZ-28	0.0005	0.001	0.0025	0.0050	0.010
BZ-31	0.0005	0.001	0.0025	0.0050	0.010
BZ-37	0.0005	0.001	0.0025	0.0050	0.010
BZ-44	0.0005	0.001	0.0025	0.0050	0.010
BZ-49	0.0005	0.001	0.0025	0.0050	0.010
BZ-52	0.0005	0.001	0.0025	0.0050	0.010
BZ-66	0.0005	0.001	0.0025	0.0050	0.010
BZ-70	0.0005	0.001	0.0025	0.0050	0.010
BZ-74	0.0005	0.001	0.0025	0.0050	0.010
BZ-77	0.0005	0.001	0.0025	0.0050	0.010
BZ-81	0.0005	0.001	0.0025	0.0050	0.010
BZ-87	0.0005	0.001	0.0025	0.0050	0.010
BZ-90	0.0005	0.001	0.0025	0.0050	0.010
BZ-99	0.0005	0.001	0.0025	0.0050	0.010
BZ-101	0.0005	0.001	0.0025	0.0050	0.010
BZ-105	0.0005	0.001	0.0025	0.0050	0.010
BZ-110	0.0005	0.001	0.0025	0.0050	0.010
BZ-114	0.0005	0.001	0.0025	0.0050	0.010
BZ-115	0.0005	0.001	0.0025	0.0050	0.010
BZ-118	0.0005	0.001	0.0025	0.0050	0.010
BZ-119	0.0005	0.001	0.0025	0.0050	0.010
BZ-123	0.0005	0.001	0.0025	0.0050	0.010
BZ-126	0.0005	0.001	0.0025	0.0050	0.010
BZ-128	0.0005	0.001	0.0025	0.0050	0.010
BZ-138	0.0005	0.001	0.0025	0.0050	0.010
BZ-141	0.0005	0.001	0.0025	0.0050	0.010
BZ-149	0.0005	0.001	0.0025	0.0050	0.010
BZ-151	0.0005	0.001	0.0025	0.0050	0.010
BZ-153	0.0005	0.001	0.0025	0.0050	0.010
BZ-156	0.0005	0.001	0.0025	0.0050	0.010
BZ-157	0.0005	0.001	0.0025	0.0050	0.010
BZ-158	0.0005	0.001	0.0025	0.0050	0.010
BZ-167	0.0005	0.001	0.0025	0.0050	0.010
BZ-168	0.0005	0.001	0.0025	0.0050	0.010
BZ-169	0.0005	0.001	0.0025	0.0050	0.010
BZ-170	0.0005	0.001	0.0025	0.0050	0.010
BZ-177	0.0005	0.001	0.0025	0.0050	0.010
BZ-180	0.0005	0.001	0.0025	0.0050	0.010
BZ-183	0.0005	0.001	0.0025	0.0050	0.010
BZ-184	0.0005	0.001	0.0025	0.0050	0.010
BZ-187	0.0005	0.001	0.0025	0.0050	0.010
BZ-189	0.0005	0.001	0.0025	0.0050	0.010

Table A-3
Calibration Levels ug/mL

BZ-194	0.0005	0.001	0.0025	0.0050	0.010
BZ-195	0.0005	0.001	0.0025	0.0050	0.010
BZ-201	0.0005	0.001	0.0025	0.0050	0.010
BZ-202	0.0005	0.001	0.0025	0.0050	0.010
BZ-206	0.0005	0.001	0.0025	0.0050	0.010
BZ-207	0.0005	0.001	0.0025	0.0050	0.010
BZ-209	0.0005	0.001	0.0025	0.0050	0.010
SURROGATES					
TCMX	0.00083	0.00166	0.00416	0.00833	0.01666
BZ-165	0.00083	0.00166	0.00416	0.00833	0.01666

Table A-4
LCS/Matrix Spike and Surrogate Spike levels for Congener analysis with Acid Cleanup
ng/L or µg/kg

	Aqueous	Low Level Soil	High Level Soil	Waste
BZ-8	10	1.67	8.33	50
BZ-18	10	1.67	8.33	50
BZ-28	10	1.67	8.33	50
BZ-44	10	1.67	8.33	50
BZ-49	10	1.67	8.33	50
BZ-52	10	1.67	8.33	50
BZ-66	10	1.67	8.33	50
BZ-77	10	1.67	8.33	50
BZ-87	10	1.67	8.33	50
BZ-101	10	1.67	8.33	50
BZ-105	10	1.67	8.33	50
BZ-118	10	1.67	8.33	50
BZ-126	10	1.67	8.33	50
BZ-128	10	1.67	8.33	50
BZ-138	10	1.67	8.33	50
BZ-153	10	1.67	8.33	50
BZ-156	10	1.67	8.33	50
BZ-169	10	1.67	8.33	50
BZ-170	10	1.67	8.33	50
BZ-180	10	1.67	8.33	50
BZ-183	10	1.67	8.33	50
BZ-184	10	1.67	8.33	50
BZ-187	10	1.67	8.33	50
BZ-195	10	1.67	8.33	50
BZ-206	10	1.67	8.33	50
BZ-209	10	1.67	8.33	50

Table A-4

LCS/Matrix Spike and Surrogate Spike levels for Congener analysis with Acid Cleanup
ng/L or µg/kg

	Aqueous	Low Level Soil	High Level Soil	Waste
Surrogates				
TCMX	16	2.67	13.33	80
BZ-165	16	2.67	13.33	80

Table A-5
Suggested Analytical Sequence

Initial Calibration

Injection #		
1	Solvent blank (optional)	
2-6	PCB Congener Mix 1 5-point	
7-11	PCB Congener Mix 2 5-point	
12-31	Sample 1-20 (or as many samples as can be analyzed in 12 hours	
	Solvent blank (optional)	
32	PCB Congener Mix 1	Level 3
33	PCB Congener Mix 2	Level 3
etc		

12 hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated.

1. SCOPE AND APPLICATION

This SOP Appendix describes procedures to be used when SW-846 Method 8081A is applied to the analysis of organochlorine pesticides by GC/ECD. This Appendix may also to be applied when discontinued SW-846 Method 8080A is requested, and is applicable to extracts derived from any matrix which are prepared according to the appropriate STL sample extraction SOPs. (CORP-OP-0001)

Table B-1 lists compounds which are routinely determined by this method and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

At client request, this method may also be used for the analysis of PCBs (Arochlors) in combination with pesticides, although these are normally analyzed following method 8082, as described in Appendix C of this SOP. In any event, if samples for PCB analysis do not need the acid clean up procedure, then the same injection may be used for method 8081B and 8082, assuming all calibration and QC requirements for both methods are met. Extracts that have been acid cleaned may not be analyzed for pesticides, since several of the pesticides will be degraded.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of organochlorine pesticides. The pesticides are injected onto the column and separated and detected by electron capture detection. Quantitation may be by internal or external standard methods.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for information regarding chromatographic interferences.

4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3. Sulfur will interfere and can be removed using procedures described in SOP CORP-OP-0001.

4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), and Sulfur cleanup (Method 3660). These cleanup procedures are included in SOP # CORP-OP-0001. Use or hexane / acetone as the extraction solvent (rather than hexane / methylene chloride) will reduce the amount of interferences extracted.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.3. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.

5.4. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Director, EH&S shall be immediately notified and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A ^{63}Ni electron capture detector is required.

6.2. Refer to Table B-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies.

7.2. Refer to Table B-3 for details of calibration standards.

7.3. Surrogate Standards

Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Refer to tables B-5 and B-6 for details of surrogate standards.

7.4. Column Degradation Evaluation Mix

A mid-level standard containing 4,4'-DDT and Endrin and not containing any of their breakdown products must be prepared for evaluation of degradation of these compounds by the GC column and injection port. This mix must be replaced after one year, or whenever corrective action to columns fails to eliminate the breakdown of the compounds, whichever is shorter. This solution also contains the surrogates. Refer to Table B-4 for details of the column degradation evaluation mix.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Refer to Table B-2 for details of GC operating conditions. The conditions listed should result in resolution of all analytes listed in Table B-1 on both columns. Closely eluting pairs are DDE and Dieldrin on the Rtx-5 or DB-5 column and Endosulfan II and DDD on the 1701 column.

10.3. Column Degradation Evaluation

Before any calibration runs, either initial or 12 hour, The column evaluation mix must be injected before each initial or daily calibration. The degradation of DDT and endrin must be calculated (see equations 9 and 10) and each shown to be less than 15% before calibration can proceed. This

is only necessary if the target compound list includes DDT, Endrin, or any of their degradation products.

If the breakdown of DDT and/or endrin exceeds the limits given above, corrective action must be taken. This action may include:

- Replacement of the injection port liner or the glass wool.
- Cutting off a portion of the injection end of a capillary column.
- Replacing the GC column.

10.4. Initial Calibration

Refer to Section 10 of the 8000B section of this SOP for details of calibration procedures.

10.4.1. Refer to Table B-8 for the initial calibration analytical sequence.

10.4.2. The response for each single-peak analyte will be calculated by the procedures described in the general method for GC analysis.

10.4.3. The surrogate calibration curve is calculated from the Individual AB mix. Surrogates in the other calibration standards are used only as retention time markers. If there are resolution problems, then the A and B mixes may be analyzed separately.

10.4.4. For multi-component pesticides:

Single point calibration is used for multicomponent pesticides (typically toxaphene and technical chlordane). Two options are possible; the same quantitation option must be used for standards and samples. Refer to section 12.3 for guidance on which option to use.

10.4.5. For multicomponent analytes, the mid level standard must be analyzed as part of the initial calibration. This single point calibration is used to quantitate multicomponent analytes.

10.4.6. The analyst may include a full 5 point calibration for any of the multicomponent analytes with the initial calibration.

10.5. 12 hour Calibration Verification

The 12 hour calibration verification sequence must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration. A mid level calibration standard is used for the 12 hour calibration. Refer to the 8000B section of this SOP for acceptance criteria.

10.5.1. At a minimum, the 12 hour calibration includes analysis of the breakdown mix followed by mid level standards of any single and multicomponent analytes.

10.5.2. The retention time windows for any analytes included in the 12 hour calibration are updated.

10.6. Continuing Calibration

The AB calibration mix is analyzed as the continuing calibration standard. At a minimum, this is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. If 12 hours elapse analyze the 12 hour standard sequence instead. The continuing calibration standard need not include multicomponent analytes. If instrument drift is expected due to sample matrix or other factors, it may be advisable to analyze the continuing calibration standard more frequently.

10.6.1. A mid level calibration standard is used for the continuing calibration.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP No. CORP-OP-0001.

11.3. Cleanup

Cleanup procedures are described in SOP No. CORP-OP-0001.

11.4. Suggested gas chromatographic conditions are given in Table B-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table B-8.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

12.2. Identification of Multicomponent Analytes

Retention time windows are also used for identification of multi-component analytes, but the "fingerprint" produced by major peaks of those compounds in the standard is used in tandem with the retention times to identify the compounds. The ratios of the areas of the major peaks are also taken into consideration. Identification of these compounds may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

12.3. Quantitation of Multicomponent Analytes

Use 3-10 major peaks or total area for quantitation as described in section 10.4.4, initial calibration of multicomponent analytes.

12.3.1. If there are no interfering peaks within the envelope of the multicomponent analyte, the total area of the standards and samples may be used for quantitation. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area.

12.3.1.1. Multiple peak option

This option is particularly valuable if toxaphene is identified but interferences make quantitation based on total area difficult. Select 3-10 major peaks in the analyte pattern. Calculate the response using the total area or total height of these peaks. Alternatively, find the response of each of the 3-10 peaks per multi-peak pesticide, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be coeluting with contaminant peaks from the quantitation. (i.e. peaks which are significantly larger than would be expected from the rest of the pattern.)

Chlordane may be quantitated either using the multiple peak option (12.3.1.1) total area option (12.3.1.2.) or by quantitation of the major components, α-chlordane, γ-chlordane and heptachlor.

12.3.1.2. Total area option

The total area of the standards and samples may be used for quantitation of multicomponent analytes. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area. This option should not be used if there are significant interference peaks within the multicomponent pattern in the samples. The retention time window for total area measurement must contain at least 90% of the area of the analyte.

12.4. Second column confirmation multi-component analytes will only be performed when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of analyte presence.

12.5. Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB) unless it is determined that sample interference has adversely affected the quantitation of that surrogate. Tetrachloro-m-xylene (TCMX) recovery is reported in lieu of DCB in samples having the interference, and also may be used in samples in which DCB recovery is low. Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits.

12.6. Calculation of Column Degradation/% Breakdown (%B)

$$DDT\ \%B = \frac{A_{DDD} + A_{DDE}}{A_{DDD} + A_{DDE} + A_{DDT}} x\ 100$$

where:
A_{DDD}, A_{DDE}, and A_{DDT} = the response of the peaks for 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT in the column degradation evaluation mix.

$$Endrin\ \%B = \frac{A_{EK} + A_{EA}}{A_{EK} + A_{EA} + A_{E}} x\ 100$$

where:
A_{EK}, A_{EA}, and A_E = the response of endrin ketone, endrin aldehyde, and endrin in the column degradation evaluation mix.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the main body of this SOP are presented in Table B-7. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

SW846, Update III, December 1996, Method 8081A

17. MISCELLANEOUS

17.1. Modifications from Reference Method

None

17.2. Modifications from Previous Revisions

17.2.1. No revisions were made to this appendix.

17.3. Tables

Table B-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, µg/L or µg/kg		
	water	soil	waste
Aldrin	0.05	1.7	50
α-BHC	0.05	1.7	50
β-BHC	0.05	1.7	50
δ-BHC	0.05	1.7	50
γ-BHC (Lindane)	0.05	1.7	50
α-Chlordane	0.05	1.7	50
γ-Chlordane	0.05	1.7	50
Chlordane (technical)	0.5	17	500
4,4'-DDD	0.05	1.7	50
4,4'-DDE	0.05	1.7	50
4,4'-DDT	0.05	1.7	50
Dieldrin	0.05	1.7	50
Endosulfan I	0.05	1.7	50
Endosulfan II	0.05	1.7	50
Endosulfan Sulfate	0.05	1.7	50
Endrin	0.05	1.7	50
Endrin Aldehyde	0.05	1.7	50
Heptachlor	0.05	1.7	50
Heptachlor Epoxide	0.05	1.7	50
Methoxychlor	0.1	3.3	100
Toxaphene	2.0	67	2000
APPENDIX IX ADD ONs			
Diallate	1.0	33	1000
Isodrin	0.1	3.3	100
Chlorobenzillate	0.1	3.3	100
Kepone[1]	1.0	33	1000

[1] Kepone is sometimes requested for analysis by method 8081A. However kepone may produce peaks with broad tails that elute later than the standard by up to a minute (presumably due to hemi-acetal formation). As a result kepone analysis by 8081A is unreliable and not recommended. Analysis by method 8270C is a possible alternative. Note: alpha chlordane, gamma chlordane, and endrin ketone are not required for some projects.

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.
Ground water	1000 mL	10 mL
Low-level Soil	30 g	10 mL
High-level soil / waste	1 g	10 mL

Table B-2	
Parameter	**Recommended Conditions**
Injection port temp	220°C
Detector temp	325°C
Temperature program	120°C for 1 min, 8.5°C/min to 285°C, , 6 min hold
Column 1	Rtx-CLPesticides 30m x 0.32mm id, 0.5µm
Column 2	Rtx-35 30m x 0.32 mm id, 0.5µm
Column 3	DB-608, 30m X 0.32 mm, 0.25µm
Injection	2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

Table B-3						
Calibration Levels ng/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6[2]
Individual Mix AB[1]						
Aldrin	5	10	25	50	100	200
g-BHC (Lindane)	5	10	25	50	100	200
Heptachlor	5	10	25	50	100	200
Methoxychlor	10	20	50	100	200	400
Dieldrin	5	10	25	50	100	200
Endosulfan I	5	10	25	50	100	200
Endosulfan II	5	10	25	50	100	200
4,4`-DDT	5	10	25	50	100	200
Endrin Aldehyde	5	10	25	50	100	200
Endrin Ketone	5	10	25	50	100	200
β-BHC	5	10	25	50	100	200
δ-BHC	5	10	25	50	100	200
α-BHC	5	10	25	50	100	200
4,4'-DDD	5	10	25	50	100	200
4,4'-DDE	5	10	25	50	100	200
Endosulfan Sulfate	5	10	25	50	100	200
Endrin	5	10	25	50	100	200
α-Chlordane [3]	5	10	25	50	100	200
γ-Chlordane [3]	5	10	25	50	100	200
Multicomponent Standards						
Chlordane (Technical)			250[4]			
Toxaphene			1000[5]			
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	5	10	25	50	100	200
Decachlorobiphenyl	5	10	25	50	100	200

[1] Standards may be split into an A and B mix if resolution of all compounds on both columns is not obtained.

[2] Level 6 is optional and should only be used if linearity can be maintained on the instrument to this level.

[3] Compounds may be used in lieu of running a daily technical Chlordane standard for samples that are non-detect for technical Chlordane.

[4] This standard may be used for quantitation of technical chlordane between 50 and 1000 ng/mL. If the chlordane is more concentrated, the extract must be diluted and reanalyzed.

[5] This standard may be used for quantitation of toxaphene between 200 and 4000 ng/mL. If the toxaphene is more concentrated, the extract must be diluted and reanalyzed.

Table B-4	
Column Degradation Evaluation Mix ng/mL	
Component	Concentration
4,4'-DDT	25
Endrin	25
Tetrachloro-m-xylene (Surrogate)	20
Decachlorobiphenyl (Surrogate)	20

Table B-5			
LCS/Matrix Spike and Surrogate Spike levels µg/L or µg/kg			
	Aqueous	Soil	Waste
gamma BHC (Lindane)	0.20	6.67	200
Aldrin	0.20	6.67	200
Heptachlor	0.20	6.67	200
Dieldrin	0.50	16.7	500
Endrin	0.50	16.7	500
4,4'DDT	0.50	16.7	500
Tetrachloro-m-xylene (Surrogate)	0.20	6.67	200
Decachlorobiphenyl (Surrogate)	0.20	6.67	200

Table B-6		
LCS/Matrix Spike and Surrogate Spike levels for TCLP µg/L or µg/kg		
	Aqueous	Waste
Heptachlor	5	500
Heptachlor epoxide	5	500
Lindane	5	500
Endrin	5	500
Methoxychlor	10	1000

Table B-7
Suggested Analytical Sequence

Initial Calibration

Solvent blank (optional)	
Breakdown Mix	
Individual mix AB	All levels
Technical Chlordane	Level 3[1]
Toxaphene	Level 3[1]
Solvent blank	
Up to 20 samples unless 12 hours comes first)	
Solvent blank (optional)	
Individual mix AB	Mid level (Continuing calibration)
Samples	
After 12 hours:	
Breakdown mix	
Individual mix AB	
Any other single component analytes	
Any multicomponent analytes	

[1] A five point curve for any of the multicomponent analytes may be included
If Arochlors are included, a 5 point calibration for Arochlor 1016/1260 should be included with the initial calibration and a single point for the other Arochlors. The mid point 1016/1260 mix is included with the daily calibration (every 12 hours).

12 hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Individual mix AB, and the breakdown mix must be run before the continuing calibration.

Table B-8		
Performance limits, four replicate initial demonstration of capability		
Compound	Initial demonstration, mean recovery limits	Initial demonstration, RSD limits
Aldrin	46-112	21
alpha-BHC	51-122	24
beta-BHC	61-120	32
delta-BHC	49.5-118.5	36
gamma-BHC	57-116	23
Chlordane	44.8-108.6	20
4,4'-DDD	52-126	28
4,4'-DDE	46-120	27.5
4,4'-DDT	54-137	36
Dieldrin	42.5-124.5	38
Endosulfan I	43-141	24.5
Endosulfan II	78-171	61
Endosulfan Sulfate	62-132	27
Endrin	49-126	37
Heptachlor	57-100	20
Heptachlor Epoxide	43.5-131.5	25.4
Toxaphene	44.4-111.2	20

1. SCOPE AND APPLICATION

1.1. This SOP Appendix describes procedures to be used when SW-846 Method 8000B is applied to the analysis of polychlorinated biphenyls (PCB) by GC/ECD. This Appendix is to be applied when SW-846 Method 8082 is requested, and is applicable to extracts derived from any matrix which are prepared according to the appropriate STL sample extraction SOPs. (CORP-OP-0001). The PCBs are determined and quantitated as Arochlor mixes.

Table C-1 lists compounds which are routinely determined by this method and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

Note: SW-846 method 8082 provides incomplete guidance for determination of individual PCB congeners. This SOP does not include directions for congener specific analysis.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of PCBs. The PCBs are injected onto the column and separated and detected by electron capture detection. Quantitation is by the external standard method.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for information regarding chromatographic interferences.

4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3. Sulfur will interfere and can be removed using procedures described in SOP CORP-OP-0001.

4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), and Sulfur cleanup (Method 3660). These cleanup procedures are included in SOP # CORP-OP-0001.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.3. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.

5.4. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Director, EH&S shall be immediately notified and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A ^{63}Ni electron capture detector is required.

6.2. Refer to Table C-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies. All standards for this method must be replaced

7.2. Refer to Table C-3 for details of calibration standards.

7.3. Surrogate Standards

Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Other surrogates may be used at client request. Refer to Table C-4 for details of surrogate standards.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Initial Calibration

10.2.1. Refer to Table C-5 for the initial calibration analytical sequence.

10.2.2. The response for each Arochlor will be calculated by the procedures described in the general method for GC analysis, with the following modifications.

10.2.3. A five point calibration of the Arochlor 1016/1260 mix is generated with at least mid level single points for the other Aroclor mixes. The average response factor is used to quantitate Arochlors 1260 and 1016, other Arochlors are quantitated from the mid level single point.

10.2.4. The analyst may include a full 5 point calibration for any of the Arochlors with the initial calibration.

10.2.5. The high and low standards for the initial 5 point calibration of 1016 / 1260 define the acceptable quantitation range for the other Arochlors. If any Arochlor is determined above this concentration the extract must be diluted and reanalyzed.

10.2.6. If the analyst knows that a specific Arochlor is of interest for a particular project, that Arochlor may be used for the five point calibration rather than the 1016 / 1260 mix.

10.2.7. The surrogate calibration curve is calculated from the Aroclor 1016/1260 mix. Surrogates in the other calibration standards are used only as retention time markers.

10.2.8. Two options are possible for quantitation of Aroclors. The same quantitation option must be used for standards and samples.

10.2.8.1. Multiple peak option

Select 3-10 major peaks in the analyte pattern. Calculate the response using the total area or total height of these peaks. Alternatively, find the response of each of the 3-10 peaks per Aroclor, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be coeluting with contaminant peaks from the quantitation. (i.e. peaks which are significantly larger than would be expected from the rest of the pattern.)

10.2.8.2. Total area option

The total area of the standards and samples may be used for quantitation of multicomponent analytes. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area. This option should not be used if there are significant interference peaks within the multicomponent pattern in the samples. The retention time window for total area measurement must contain at least 90% of the area of the analyte.

10.3. 12 hour Calibration

The 12 hour calibration verification must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration.

10.3.1. At a minimum, the 12 hour calibration includes analysis of the Arochlor 1260 / 1016 mix.

10.3.2. It is adequate to verify calibration with a mixture of Aroclors 1016 and 1260. If a specific Aroclor is expected, it should be included in the daily calibration check.

10.3.3. The retention time windows for any analytes included in the daily calibration are updated.

10.3.4. For this method samples must be bracketed with successful calibration verification runs.

10.4. Calibration verification

The Arochlor 1260/1016 calibration mix is analyzed as the calibration verification standard. This is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. (Depending on the type of samples, it may be advisable to analyze verifications more frequently in order to minimize reruns.).

10.4.1. A mid level standard is used for the calibration verification.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP No. CORP-OP-0001.

11.3. Cleanup

Cleanup procedures are described in SOP No. CORP-OP-0001.

11.4. Suggested gas chromatographic conditions are given in Table C-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table C-5.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Identification of Arochlors

Retention time windows are used for identification of Arochlors, but the "fingerprint" produced by major peaks of those analytes in the standard is used in tandem with the retention times for identification. The ratios of the areas of the major peaks are also taken into consideration. Identification may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

A clearly identifiable Arochlor pattern serves as confirmation of single column GC analysis. However, if the pattern is not clear, or if no historical data for the site is available, then second column confirmation must be performed.

12.2. Quantitation of Arochlors

Use 3-10 major peaks or total area for quantitation

If the analyst believes that a combination of Aroclor 1254 and 1260, or a combination of 1242, 1248 and 1232 is present, then only the predominant Arochlor is quantitated and reported, but the suspicion of multiple Aroclors is discussed in the narrative. If well separated, Aroclor patterns are present, then both Aroclors are quantitated and reported.

12.2.1 Laboratory uses 3-5 major peaks.

12.3. If there are no interfering peaks within the envelope of the Arochlor, the total area of the standards and samples may be used for quantitation. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area.

12.4. Second column confirmation of Aroclors will only be performed when requested by the client, or if the pattern is not clear or there is no historical data leading to a suspicion that Arochlors may be present. The appearance of the multiple peaks in the sample usually serves as a confirmation of Aroclor presence.

12.5. Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB) unless it is determined that sample interference has adversely affected the quantitation of that surrogate. Tetrachloro-m-xylene (TCMX) recovery is reported in lieu of DCB in samples having the interference, and also may be used in samples in which DCB recovery is low. Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the main body of this SOP are recovery of 70-130%. The spiking level should be equivalent to a mid level calibration.

13.2. Method detection limits (MDL) are determined for Arochlor 1016 and 1260. Arochlor 1016 represents an Arochlor consisting primarily of low chlorinated congeners while Arochlor 1260 represents an Arochlor consisting primarily of high chlorinated congeners. The same reporting limit is applied to all Arochlors, and must be supported by both MDLs.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

SW846, Update III, December 1996, Method 8082

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Method 8082 includes limited direction for congener specific quantitation. This is outside the scope of this SOP.

17.2. Modifications from Previous Revisions

No changes were made to this Appendix

17.3. Tables

Table C-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, µg/L or µg/kg		
	water	soil	waste
Aroclor-1016	1.0	33	1000
Aroclor-1221	1.0	33	1000
Aroclor-1232	1.0	33	1000
Aroclor 1242	1.0	33	1000
Aroclor-1248	1.0	33	1000
Aroclor-1254	1.0	33	1000
Aroclor-1260	1.0	33	1000

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.
Ground water	1000 mL	10 mL
Low-level Soil	30 g	10 mL
High-level soil / waste	1 g	10 mL

Table C-2

Parameter	Recommended Conditions
Injection port temp	220°C
Detector temp	325°C
Temperature program	70°C for 0.5min, 30°C/min to 190°C, 2.5°C/min to 225, 18°C/min to 280°C, 3 min hold
Column 1	DB-5 or Rtx-5 30m x 0.32mm id, 0.5µm
Column 2	DB-1701 or Rtx 1701 30m x 0.32 mm id, 0.25µm
Column 3	DB-608, 30m X 0.32 mm, 0.25µm
Injection	1-2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

Table C-3						
Calibration Levels ng/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6[1]
Aroclor 1016/1260	100	200	500	1000	2000	4000
Aroclor 1242[2]			500			
Aroclor 1221 +1254[2]			500			
Aroclor 1232[2]			500			
Aroclor 1248[2]			500			
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	5	10	25	50	100	200
Decachlorobiphenyl	5	10	25	50	100	200

[1] Level 6 is optional and should only be used if linearity can be maintained on the instrument to this level.

[2] Aroclors may be quantitated within the range 100 to 2000 ng/mL (4000ng/mL if the level 6 1016/1260 standard is included). If the Aroclor is more concentrated, it must be reanalyzed at a dilution.

Table C-4			
LCS/Matrix Spike and Surrogate Spike levels for Aroclor analysis with Acid Cleanup µg/L or µg/kg			
	Aqueous	Soil	Waste
Aroclor 1016/1260	10	333	10,000
Tetrachloro-m-xylene (Surrogate)	0.20	6.67	200
Decachlorobiphenyl (Surrogate)	0.20	6.67	200

Table C-5
Suggested Analytical Sequence

Initial Calibration

Injection #		
1	Solvent blank (optional)	
2	Aroclor 1016/1260	Level 1
3	Aroclor 1016/1260	Level 2
4	Aroclor 1016/1260	Level 3
5	Aroclor 1016/1260	Level 4
6	Aroclor 1016/1260	Level 5
7	Aroclor 1232	Level 3
8	Aroclor 1242	Level 3
9	Aroclor 1248	Level 3
10	Aroclor 1221/1254	Level 3
11	Solvent blank	
12-31	Sample 1-20 (or as many samples as can be analyzed in 12 hours	
	Solvent blank (optional)	
32	Aroclor 1016/1260	Level 3

etc

12 hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Aroclor 1260 / 1016 mix. Mid level standards of any other Aroclors expected to be present in the samples are also injected.

1. SCOPE AND APPLICATION

This method is applicable to the gas chromatographic determination of Chlorinated phenoxy acid herbicides in extracts prepared by SOP CORP-OP-0001. The herbicides listed in Table D1 are routinely analyzed. Other chlorinated acids may be analyzed by this method if the quality control criteria in section 9 and the initial demonstration of method performance in section 13 are met.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of phenoxy acid herbicides by gas chromatography. The herbicides, as their methyl esters, are injected onto the column, separated, and detected by electron capture detectors. Quantitation is by the external standard method.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for general information regarding chromatographic interferences.

4.2. Chlorinated acids and phenols cause the most direct interference with this method.

4.3. Sulfur may interfere and may be removed by the procedure described in SOP#CORP-OP-0001.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A Ni_{63} electron capture detector is required.

6.2. Refer to Table D2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to section 7 of the 8000B section of this SOP for general information on reagents and standards.

7.2. Refer to Table D-3 and D-4 for details of calibration and other standards.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

Refer to section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

9.2. Refer to Table D-5 for minimum performance criteria for the initial demonstration of capability.

9.3. Refer to Table D-4 for the components and levels of the LCS and MS mixes.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Calibration standards are made up from the free acids, and then esterified using the same process as for samples (See SOP Corp-OP-0001)

10.3. The low level standard must be at or below the laboratory reporting limit. Other standards are chosen to bracket the expected range of concentrations found in samples, without saturating the detector or leading to excessive carryover.

10.4. Refer to Table D-2, for details of GC operating conditions.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP #CORP-OP-0001.

11.3. Cleanup

The alkaline hydrolysis and subsequent extraction of the basic solution described in the extraction procedure provides an effective cleanup.

11.4. Analytical Sequence

The analytical sequence starts with an initial calibration of at least five points, or a daily calibration that meets % difference criteria from an existing initial calibration.

11.4.1. The daily calibration must be analyzed at least once every 24 hours when samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 24 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a daily calibration.

11.4.2. The daily calibration consists of mid level standards of all analytes of interest. Retention time windows must be updated with the daily calibration.

11.4.3. After every 12 hours a continuing calibration is analyzed. The continuing calibration consists of mid level standards of all analytes of interest. Retention time windows are updated with continuing calibrations.

11.5. Gas Chromatography

Chromatographic conditions are listed in Table D-2.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

12.2. The herbicides are analyzed as their methyl esters, but reported as the free acid. For this reason it is necessary to correct the results for the molecular weight of the ester versus the free acid. This is achieved through the concentrations of the calibration standards. For example the 20µg/L calibration standard for 2,4-D contains 21.3 µg/L of the methyl ester. No further correction is necessary.

Standard Analyte list
Weight Corrections

Compound	*CAS Number*	*Molecular weight(g/mol)*	
		Acid	*Methyl Ester*
2,4-D	*94-75-7*	*221.0*	*235.1*
2,4-DB	*94-82-6*	*249.1*	*263.1*
2,4,5-TP (Silvex)	*93-72-1*	*269.5*	*283.5*
2,4,5-T	*93-76-5*	*255.5*	*269.5*
Dalapon	*75-99-0*	*143.0*	*157.0*
Dicamba	*1918-00-9*	*221.0*	*235.1*
Dichloroprop	*120-36-5*	*235.1*	*249.1*
Dinoseb	*88-85-7*	*240.2*	*254.2*
MCPA	*94-74-6*	*200.6*	*214.6*
MCPP	*7085-19-0*	*214.6*	*228.6*

13. METHOD PERFORMANCE

13.1. Multiple laboratory performance data has not been published by the EPA for this method. Table D-5 lists minimum performance standards required by STL for the four replicate initial demonstration or capability (required by Section 13.2 of the 8000B part of this SOP) for this method. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

Method 8151A, SW-846, Update III, December 1996

17. MISCELLANEOUS

17.1. Modifications from Reference Method

Refer to the method 8000B section of this SOP for modifications from the reference method.

17.2. Modifications from Previous Revision

The calibration procedure has been changed to require esterification of the calibration standards

17.3. Tables

Table D-1					
Standard Analyte list					
Compound	CAS Number	Reporting Limit, µg/L or µg/kg			
		Aqueous	Soil	Waste	TCLP
2,4-D	94-75-7	4	80	4000	500
2,4-DB	94-82-6	4	80	4000	---
2,4,5-TP (Silvex)	93-72-1	1	20	1000	500
2,4,5-T	93-76-5	1	20	1000	---
Dalapon	75-99-0	2	40	2000	---
Dicamba	1918-00-9	2	40	2000	---
Dichloroprop	120-36-5	4	80	4000	---
Dinoseb	88-85-7	0.6	12	600	---
MCPA	94-74-6	400	8000	400,000	---
MCPP	93-65-2	400	8000	400,000	---

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.	Dilution Factor
Ground water	1000 mL	10 mL	20
Low-level Soil without GPC	50 g	10 mL	20
High-level soil / waste	1 g	10 mL	20

Specific reporting limits are highly matrix dependent. The reporting limits listed above are provided for guidance only and may not always be achievable. For special projects, the extracts may be analyzed without any dilution, resulting in reporting limits 20 times lower than those in Table D-1.

Table D-2	
Instrumental Conditions	
PARAMETER	Recommended conditions
Injection port temp	220°C
Detector temp	325°C
Temperature program	80,2/30/170,0/1/180,1
Column 1	DB-5MS or RTX 5 30x0,32, 0.5um
Column 2	DB-1701 or Rtx-1701
Injection	1-2µL
Carrier gas	Helium / Hydrogen
Make up gas	Nitrogen

Recommended conditions should result in resolution of all analytes listed in Table D-1.

The reporting limits listed in Table D-1 will be achieved with these calibration levels and a 20 fold dilution of the sample extract. Lower reporting limits can be achieved with lesser dilutions of the sample extract.

Table D-3				
LCS/Matrix Spike and Surrogate Spike levels µg/L or µg/kg[1]				
	Aqueous	Soil	Waste	TCLP
2,4-D	16	800	16000	6ug/L ; 120ug/kg
Silvex	4	200	4000	6ug/L ; 120ug/kg
2,4,5-T	4	200	4000	6ug/L ; 120ug/kg
2,4-DB	16	800	16000	---
Dalapon	8	400	8000	---
DCAA (surrogate)	16	800	16000	10ug/L;500ug/kg

[1] LCS, MS and SS spikes are as the free acid.

Table D-4		
Performance limits, four replicate initial demonstration of capability		
Compound	Initial demonstration, mean recovery limits	Initial demonstration, RSD limits
2,4-D	50-150	25
2,4-DB	50-150	25
2,4,5-TP (Silvex)	50-150	25
2,4,5-T	50-150	25
Dalapon	50-150	25
Dicamba	50-150	25
Dichloroprop	50-150	25
Dinoseb	25-120	40
MCPA	50-150	25
MCPP	50-150	25

Table D-5					
Calibration Levels					
Compound	Concentration levels in ug/ml				
2,4-D	0.0211	0.0425	0.0851	0.1700	0.3400
DCAA	0.0213	0.0425	0.0851	0.1700	0.3400
2,4-DB	0.0211	0.0422	0.0845	0.1690	0.3380
2,4,5-TP (Silvex)	0.0053	0.0105	0.0211	0.0421	0.0840
2,4,5-T	0.0053	0.0105	0.0211	0.0422	0.0844
Pentachlorophenol	0.0027	0.0053	0.0106	0.0213	0.0425
Dalapon	0.0110	0.0220	0.0439	0.0878	0.1760
Dicamba	0.0106	0.0213	0.0425	0.0851	0.1700
Dichloroprop	0.0212	0.0424	0.0848	0.1700	0.3390
MCPP	2.120	4.260	8.520	17.00	34.10
Dinoseb	0.0032	0.0063	0.0127	0.0254	0.0508
MCPA	2.140	4.280	8.560	17.10	34.00

1. SCOPE AND APPLICATION

1.1. This SOP Appendix describes procedures to be used when SW-846 Method 8141 is applied to the analysis of organophosphorous pesticides by GC/FPD. This Appendix is applicable to extracts derived from any matrices which are prepared according to the appropriate STL sample extraction SOPs. (C-OP-0001)

1.2. Table B-1 lists compounds which are routinely determined by this method and their associated Reporting Limits (RL) for each matrix. RLs given are based on the low-level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

2. SUMMARY OF METHOD

2.1. This method presents conditions for the analysis of prepared extracts of organophosphorous pesticides. The pesticides are injected onto the column and separated and detected by Flame Photometric detection. Quantitation may be by internal or external standard methods.

3. DEFINITIONS

3.1. Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for information regarding chromatographic interferences.

4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the flame photometric detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding sample/reagent contact with plastic materials.

4.3. Sulfur will interfere and can be removed using procedures described in SOP C-OP-0001.

4.4. Interferences extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups have not been determined for this method.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A flame photometric detector is required.

6.2. Refer to Table B-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies.

7.2. Refer to Table B-3 for details of calibration standards.

7.3. Surrogate Standards

Triphenyl phosphate and Tributyl phosphate are the surrogate standards. Refer to tables B-5 and B-6 for details of surrogate standards.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Refer to Table B-2 for details of GC operating conditions. The conditions listed should result in resolution of all analytes listed in Table B-1 using both columns.

10.3. Initial Calibration

Refer to Section 10 of the 8000B section of this SOP for details of calibration procedures.

10.3.1. Refer to Table B-7 for the initial calibration analytical sequence.

10.3.2. The response for each single-peak analyte will be calculated by the procedures described in the general method for GC analysis.

10.4. 12 hour Calibration Verification

The 12 hour calibration verification sequence must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration. A mid level calibration standard is used for the 12 hour calibration. Refer to the 8000B section of this SOP for acceptance criteria.

10.4.1. The retention time windows for any analytes included in the 12 hour calibration are updated.

10.5. Continuing Calibration

The mid-level calibration mix is analyzed as the continuing calibration standard. At a minimum, this is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. If 12 hours elapse analyze the 12 hour standard sequence instead. If instrument drift is expected due to sample matrix or other factors, it may be advisable to analyze the continuing calibration standard more frequently.

10.5.1. A mid level calibration standard is used for the continuing calibration.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP No. C-OP-0001.

11.3. Cleanup

No cleanup procedure has been determined.

11.4. Suggested gas chromatographic conditions are given in Table B-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table B-7.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

12.2. Surrogate recovery results are calculated and reported for Triphenyl phosphate and Tributylphosphate. Corrective action is only necessary if Triphenyl phosphate and Tributyl phosphate are both outside of acceptance limits.

13. METHOD PERFORMANCE

13.1. Current laboratory performance limits are listed in Tables B-5a and B-5b. The spiking level should be equivalent to a mid-level calibration.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

SW846, Update III, December 1996, Method 8141A

17. MISCELLANEOUS

17.1. Modifications from Reference Method

None

17.2. Modifications from Previous Revisions

17.2.1. No revisions were made to this appendix.

17.3. Tables

AK5 042006

Table B-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, µg/L or µg/kg	
	water	soil
Dimethoate	1	33
Disulfoton	1	33
Famphur	1	33
Methyl parathion	1	33
O,O,O-Triethyl phosphorothioate	1	33
Parathion	1	33
Phorate	1	33
Tetraethyldithiopyrophosphate	1	33
Thionazin	1	33
Azinphos-methyl	1	33
Bolstar	1	33
Chlorpyrifos	1	33
Coumaphos	1	33
Demeton (total)	1	100
Demeton-O	1	33
Demeton-S	1	33
Diazinon	1	33
Dichlorvos	1	33
EPN	1	33
Ethoprop	1	33
Ethyl parathion	1	33
Fensulfothion	1	33
Fenthion	1	33
Malathion	1	33
Merphos	1	33
Mevinphos	1	33
Monocrotophos	1	33
Naled	1	33
Ronnel	1	33
Stirophos	1	33
Sulfotepp	1	33
Tokuthion	1	33
Trichloronate	1	33

Table B-2	
Parameter	**Recommended Conditions**
Injection port temp	220°C
Detector temp	250°C
Temperature program	110C for .5 min, 3.0°C/min to 250°C, , 2.84 min hold
Column 1	DB608 30m x 0.53mm id, 1µm
Column 2	DB1701 30m x 0.53 mm id, 1µm
Injection	2µL
Carrier gas	Helium
Make up gas	Helium

Table B-3					
Calibration Levels ng/mL					
	Level 1	Level 2	Level 3	Level 4	Level 5
Dimethoate	.2	.5	1.0	2.0	4.0
Disulfoton	.2	.5	1.0	2.0	4.0
Famphur	.2	.5	1.0	2.0	4.0
Methyl parathion	.2	.5	1.0	2.0	4.0
O,O,O-Triethyl phosphorothioate	.2	.5	1.0	2.0	4.0
Parathion	.2	.5	1.0	2.0	4.0
Phorate	.2	.5	1.0	2.0	4.0
Tetraethyldithiopyrophosphate	.2	.5	1.0	2.0	4.0
Thionazin	.2	.5	1.0	2.0	4.0
Tributyl phosphate	.2	.5	1.0	2.0	4.0
Triphenyl phosphate	.2	.5	1.0	2.0	4.0
Azinphos-methyl	.2	.5	1.0	2.0	4.0
Bolstar	.2	.5	1.0	2.0	4.0
Chlorpyrifos	.2	.5	1.0	2.0	4.0
Coumaphos	.2	.5	1.0	2.0	4.0
Demeton (total)	.2	.5	1.0	2.0	4.0
Demeton-O	.2	.5	1.0	2.0	4.0
Demeton-S	.2	.5	1.0	2.0	4.0
Diazinon	.2	.5	1.0	2.0	4.0
Dichlorvos	.2	.5	1.0	2.0	4.0
EPN	.2	.5	1.0	2.0	4.0
Ethoprop	.2	.5	1.0	2.0	4.0
Ethyl parathion	.2	.5	1.0	2.0	4.0
Fensulfothion	.2	.5	1.0	2.0	4.0
Fenthion	.2	.5	1.0	2.0	4.0
Malathion	.2	.5	1.0	2.0	4.0
Merphos	.2	.5	1.0	2.0	4.0
Mevinphos	.2	.5	1.0	2.0	4.0
Monocrotophos	.2	.5	1.0	2.0	4.0
Naled	.2	.5	1.0	2.0	4.0
Ronnel	.2	.5	1.0	2.0	4.0
Stirophos	.2	.5	1.0	2.0	4.0
Sulfotepp	.2	.5	1.0	2.0	4.0
Tetraethyl pyrophosphate	.2	.5	1.0	2.0	4.0
Tokuthion	.2	.5	1.0	2.0	4.0
Trichloronate	.2	.5	1.0	2.0	4.0

1 Standards may be split into multiple mixs if resolution of all compounds on both columns is not obtained.
Note: Component mixes of a CCAL should be run sequentially. The ccal evaluation is performed on the sum of the mixes, rather than by mix. Ie. the CCAL = sum of the component mixes.

Table B-5a

Aqueous LCS/Matrix Spike and Surrogate Spike levels µg/L

		LCS		MSD	
Compound	ug/L	LCL	UCL	LCL	UCL
Dimethoate	10	46	153	70	192
Disulfoton	10	17	185	36	130
Famphur	10	14	165	59	131
Methyl parathion	10	36	159	65	157
O,O,O-Triethyl phosphorothioate	10	65	141	60	172
Parathion	10	13	150	65	144
Phorate	10	35	152	54	154
Tetraethyldithiopyrophosphate	10	75	140	51	158
Thionazin	10	69	149	56	136
Tributyl phosphate	10	30	150	30	150
Triphenyl phosphate	10	25	152	25	152

Table B-5b

Soil LCS/Matrix Spike and Surrogate Spike levels µg/mg

		LCS		MSD	
Compound	ug/kg	LCL	UCL	LCL	UCL
Dimethoate	33	65	135	45	170
Disulfoton	33	66	133	26	136
Famphur	33	42	162	31	178
Methyl parathion	33	64	144	56	150
O,O,O-Triethyl phosphorothioate	33	58	131	48	130
Parathion	33	58	141	58	145
Phorate	33	71	135	51	140
Tetraethyldithiopyrophosphate	33	69	144	63	143
Thionazin	33	68	140	64	136
Tributyl phosphate	33	30	150	30	150
Triphenyl phosphate	33	20	151	20	151

Table B-7
Suggested Analytical Sequence

Initial Calibration

Solvent blank (optional)
Calibration Mix A
Calibration Mix B
Calibration Mix C
Solvent blank
Up to 20 samples unless 12 hours comes first)
Solvent blank (optional)
Individual mix AB Mid level (Continuing calibration)
Samples
After 12 hours:

Calibration Check Mix

12 hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Individual mix AB.

Tables B8 & B9 Laboratory Control Limits and Control Compound List (STL Reference Data Summary) See Attachments: current print outs from LIMS system.

1. SCOPE AND APPLICATION

This SOP Appendix describes procedures to be used when SW-846 Method 8310 is applied to the analysis of Polynuclear Aromatic Hydrocarbons by HPLC. This Appendix is applicable to extracts derived from any matrix which are prepared according to the appropriate STL sample extraction SOPs. (C-OP-0001)

Table B-1 lists compounds which are routinely determined by this method and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of Polynuclear Aromatic Hydrocarbons. The extracts are injected onto the column and separated and detected by ultraviolet(UV) and fluorescence detection. Quantitation may be by internal or external standard methods.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for information regarding chromatographic interferences.

4.2. Interferences in the HPLC analysis arise from many compounds amenable to HPLC that give a measurable response on the UV and fluorescence detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups have not been determined for this method.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. UV and fluororescence detectors are required.

6.2. Refer to Table B-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies.

7.2. Refer to Table B-3 for details of calibration standards.

7.3. Surrogate Standards

Benzo(e)pyrene and p-terphenyl are the surrogate standards. Refer to tables B-5 for details of surrogate standards.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Refer to Table B-2 for details of HPLC operating conditions. The conditions listed should result in resolution of all analytes listed in Table B-1 on both detectors.

10.3. Initial Calibration

Refer to Section 10 of the 8000B section of this SOP for details of calibration procedures.

10.3.1. Refer to Table B-8 for the initial calibration analytical sequence.

10.3.2. The response for each single-peak analyte will be calculated by the procedures described in the general method for GC analysis.

10.4. 12 hour Calibration Verification

The 12 hour calibration verification sequence must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration. A mid level calibration standard is used for the 12 hour calibration. Refer to the 8000B section of this SOP for acceptance criteria.

10.4.1. .

10.4.2. The retention time windows for any analytes included in the 12 hour calibration are updated.

10.5. Continuing Calibration

The mid-level calibration mix is analyzed as the continuing calibration standard. At a minimum, this is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. If 12 hours elapse analyze the 12 hour standard sequence instead. If instrument drift is expected due to sample matrix or other factors, it may be advisable to analyze the continuing calibration standard more frequently.

10.5.1. A mid level calibration standard is used for the continuing calibration.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP No. C-OP-0001.

11.3. Cleanup

No cleanup procedure has been determined.

11.4. Suggested HPLC conditions are given in Table B-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table B-8.

12. DATA ANALYSIS AND CALCULATIONS

Both the fluorescence detector and the UV detector are used for qualitative determination and confirmation of the presence of target compounds, however each target compound is quantitated using only one detector. Table B-1 presents the detectors used for quantitating each compound.The MDL studies are performed on both detectors. The highest MDL will be used for reporting "J"-Values. In the instance where there is no detection of any compounds on the UV detector, the Flourescence Detector results will not be submitted.

12.1. Surrogate recovery results are calculated and reported for Benzo(e)pyrene and p-terphenyl. Corrective action is only necessary if Benzo(e)pyrene and p-terphenyl are both outside of acceptance limits.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the main body of this SOP are presented in Table B-7. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

SW846, Update III, December 1996, Method 8310

17. MISCELLANEOUS

17.1. Modifications from Reference Method

None

17.2. Modifications from Previous Revisions

17.2.1. No revisions were made to this appendix.

17.3. Tables

Table B-1
Standard Analyte list and Reporting Limits and Detectors

Compound	Reporting Limit, µg/L or µg/kg		
	water	soil	Detectors
Carbazole	1.0	33	UV/Flourescence
Naphthalene	1.0	33	UV/Flourescence
Acenaphthene	1.0	33	UV/Flourescence
Acenaphthylene	1.0	33	UV
Anthracene	.2	6.7	UV/Flourescence
Benzo(a)anthracene	.2	6.7	UV/Flourescence
Benzo(b)fluoranthene	.2	6.7	UV/Flourescence
Benzo(k)fluoranthene	.2	6.7	UV/Flourescence
Benzo(g,h,i)perylene	.2	6.7	UV/Flourescence
Benzo(a)pyrene	.2	6.7	UV/Flourescence
Chrysene	.2	6.7	UV/Flourescence
Fluoranthene	.2	6.7	UV/Flourescence
Fluorene	.2	6.7	UV/Flourescence
Indeno(1,2,3-cd)pyrene	.2	6.7	UV/Flourescence
Pyrene	.2	6.7	UV/Flourescence
Phenanthrene	.2	6.7	UV/Flourescence
Dibenzo(a,h)anthracene	.2	6.7	UV/Flourescence
1-methylnaphthalene	1.0	33	UV/Flourescence
2-methylnaphthalene	1.0	33	UV/Flourescence

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.
Ground water	1000 mL	1.0 mL
Low-level Soil	30 g	1.0 mL
High-level soil / waste	1 g	1.0 mL

Table B-2	
Parameter	**Recommended Conditions**
Mobile phase program	Time 0min:solvent A 50% solvent B 50% flow 1.5 ml/min Time 7min:solvent A 65% solvent B 35% flow 1.5 ml/min Time 10min:solvent A 75% solvent B 25% flow 1.5 ml/min Time 15min:solvent A 85% solvent B 15% flow 1.5 ml/min Time 20min:solvent A 95% solvent B 5% flow 1.5 ml/min
Column 1	Hypersil PAH 150mm x 4.6mm ID
Injection	20µL
Solvent A	CH3CN
Solvent B	H2O

Table B-3						
Calibration Levels ng/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	
Individual Mix						
Carbazole	1	4	7.5	10	20	
Naphthalene	1	4	7.5	10	20	
Acenaphthene	1	4	7.5	10	20	
Acenaphthylene	1	4	7.5	10	20	
Anthracene	.2	.8	1.5	2	4	
Benzo(a)anthracene	.2	.8	1.5	2	4	
Benzo(b)fluoranthene	.2	.8	1.5	2	4	
Benzo(k)fluoranthene	.2	.8	1.5	2	4	
Benzo(g,h,i)perylene	.2	.8	1.5	2	4	
Benzo(a)pyrene	.2	.8	1.5	2	4	
Chrysene	.2	.8	1.5	2	4	
Fluoranthene	.2	.8	1.5	2	4	
Fluorene	.2	.8	1.5	2	4	
Indeno(1,2,3-cd)pyrene	.2	.8	1.5	2	4	
Pyrene	.2	.8	1.5	2	4	
Phenanthrene	.2	.8	1.5	2	4	
Dibenzo(a,h)anthracene	.2	.8	1.5	2	4	
1-methylnaphthalene	1	4	7.5	10	20	
2-methylnaphthalene	1	4	7.5	10	20	
p-terphenyl	1	4	7.5	10	20	
Benzo(e)pyrene	1	4	7.5	10	20	

Table B-5 LCS/Matrix Spike and Surrogate Spike levels µg/L or µg/kg		
	Aqueous	Soil
Carbazole	6.25	208
Naphthalene	6.25	208
Acenaphthene	6.25	208
Acenaphthylene	6.25	208
Anthracene	1.25	41.7
Benzo(a)anthracene	1.25	41.7
Benzo(b)fluoranthene	1.25	41.7
Benzo(k)fluoranthene	1.25	41.7
Benzo(g,h,i)perylene	1.25	41.7
Benzo(a)pyrene	1.25	41.7
Chrysene	1.25	41.7
Fluoranthene	1.25	41.7
Fluorene	1.25	41.7
Indeno(1,2,3-cd)pyrene	1.25	41.7
Pyrene	1.25	41.7
Phenanthrene	1.25	41.7
Dibenzo(a,h)anthracene	1.25	41.7
1-methylnaphthalene	6.25	208
2-methylnaphthalene	6.25	208
p-terphenyl	10	333
Benzo(e)pyrene	10	333

Table B-7
Suggested Analytical Sequence

Initial Calibration

Solvent blank (optional)	
Individual mix	All levels
Solvent blank	
Up to 20 samples unless 12 hours comes first)	
Solvent blank (optional)	
Individual mix	Mid level (Continuing calibration)
Samples	
After 12 hours:	
Individual mix [1]	

12 hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Individual mix ..

Tables B8 & B9 Laboratory Control Limits and Control Compound List (STL Reference Data Summary) See Attachements: current print outs from LIMS system.

APPENDIX C
LABORATORY SOP FOR METHOD 1613

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Implementation Date: 2/28/02

SOP No.: KNOX-ID-0004
Revision No.: 2
Revision Date: 02/20/2002

STL KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: Analysis of Polychlorinated Dioxins/Furans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) Based on Method 1613B

(SUPERSEDES: KNOX-ID-0004, Rev. 1)

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1. Scope and Application

1.1 This procedure is used for the determination of tetra- through octa- chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in water, soils, solids, sediments, wipes, biological samples, fly ash, XAD resin, filters, still bottoms, waste oils, and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). This procedure is designed to meet analytical program requirements where US EPA Method 1613B is specified.

1.2 The seventeen 2,3,7,8-substituted PCDDs/PCDFs listed in Table 1 may be determined by this procedure. Specifications are also provided for separate determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF).

1.3 The detection limits and quantitation levels in this method are usually dependent on the level of interferences rather than instrumental limitations. The minimum levels (MLs) in Table 2 are the levels at which the PCDDs/PCDFs can be determined with no interferences present.

1.4 This procedure is designed for use by analysts who are experienced with residue analysis and skilled in HRGC/HRMS.

1.5 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 5 of this procedure discusses safety procedures.

2. Summary of Method

2.1 This procedure uses high resolution capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS) techniques.

2.2 Samples are spiked with a solution of known amounts of the isotopically labeled internal standards listed in column 3 of Table 1. The samples are then extracted using matrix specific extraction procedures.

2.2.1 Water samples are extracted using separatory funnel techniques with methylene chloride as the extraction solvent.

2.2.2 Solid samples are extracted by Soxhlet extraction with the appropriate solvent.

2.2.3 Waste samples are diluted in solvent.

2.3 After extraction, the sample is concentrated and solvent exchanged with hexane. The sample is then subjected to one or more cleanup steps to rid the sample of interferences. The final extract is prepared by adding a known amount of the labeled recovery standards ($^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD) and concentrating to the final volume.

2.4 The acid-base cleanup of the sample is used before column chromatography for samples that contain large amounts of basic and acid coextractables. If such interferences are not removed before column chromatography, they may cause a shift in the predicted elution pattern. Conditions which may indicate the need for this procedure are: samples which are highly colored, samples which contain lipids or other oxidizable compounds or samples which contain known large amounts of polar organics.

2.5 Silica gel is effective in removing chlorophenoxy herbicide residues, while alumina partitions PCBs, 2,4,5-trichlorophenol and hexachlorophene.

2.6 When the above cleanup techniques do not completely remove interferences, an activated carbon cleanup is used to remove interferences.

2.7 An aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high resolution (≥10,000) mass spectrometer. Two exact m/z's are monitored for each analyte.

2.8 The identification of the target 2,3,7,8 substituted isomers is based on their retention time relative to the labeled internal standards as established during routine calibration and the simultaneous detection of the two most abundant ions in the molecular ion region. All other PCDD/PCDF congeners are identified by their retention times falling within retention time windows as established during routine calibration, and the simultaneous detection of the two most abundant ions in the molecular ion region. Confirmation of identification is based on comparing the calculated ion ratios with the theoretical ion abundances.

2.9 Quantitation of the 2,3,7,8-substituted PCDD/PCDF isomers, total PCDDs, and total PCDFs is based on their relative response to the internal standards. A multipoint calibration is performed to establish mean response factors for the target analytes. The instrument performance is routinely checked by the analysis of continuing calibration standards. Method performance is demonstrated by the analysis of method blanks, initial precision and recovery samples, and ongoing precision and recovery samples.

3. Definitions

3.1 Analyte: A PCDD or PCDF tested for by this method. The analytes are listed in Table 1.

3.2 Calibration Standard: A solution prepared from a secondary standard and/or stock solution and used to calibrate the response of the instrument with respect to analyte concentration.

3.3 Calibration Verification Standard (VER): The mid-point calibration standard (CS3) that is used to verify calibration. See Table 3.

3.4 Cleanup Standard: $^{37}Cl_4$-2,3,7,8-TCDD which is added to samples, blanks, quality control samples, and calibration solutions. It is added to the samples after extraction but prior to extract cleanup, and is used to judge the efficiency of the cleanup procedures.

3.5 Column Performance Solution Mixture (CPSM): A mixture of TCDD or TCDF isomers (including the 2,3,7,8-TCDD or 2,3,7,8-TCDF isomer) known to elute close to the retention

time of 2,3,7,8-TCDD or 2,3,7,8-TCDF on the analytical column being used. It is used to demonstrate acceptable resolution between the 2,3,7,8-TCDD or 2,3,7,8-TCDF isomer and all other TCDD or TCDF isomers on analytical column (percent valley $\leq$ 25%).

3.6 Congener: Any member of a particular homologous series, for example, 1,2,3,7,8-pentachlorodibenzofuran.

3.7 CS1, CS2, CS3, CS4, CS5: See Calibration Standard and Table 3.

3.8 Detection Limit (D.L.): The minimum concentration of the target analyte that can be detected. Sample specific detection limits are calculated from the instrument noise level and internal standard response.

3.9 Estimated Detection Limit (EDL.): The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level.

3.10 Estimated Maximum Possible Concentration (EMPC): The calculated concentration of a signal having the same retention time as a target pesticide but which does not meet the other qualitative identification criteria defined in the procedure.

3.11 GC: Gas chromatograph or gas chromatography

3.12 Homologous Series: A series of compounds in which each member differs from the next member by a constant amount. The members of the series are called homologs.

3.13 HRGC: High resolution GC

3.14 HRMS: High resolution MS

3.15 ICV: Initial Calibration Verification Standard. A calibration standard from a second source, traceable to a national standard if possible. The ICV is analyzed after the Initial calibration to verify the concentration of the Initial Calibration Standards.

3.16 Internal Standards: Isotopically labeled analogs of the target analytes that are added to every sample, blank, quality control spike sample, and calibration solution. They are added to the sample before extraction and are used to calculate the concentration of the target analytes or detection limits.

3.17 IPR: Initial precision and recovery; four aliquots of the diluted PAR standard analyzed to establish the ability to generate acceptable precision and accuracy. An IPR is performed prior to the first time this method is used and any time the method or instrumentation is modified.

3.18 Isomer: Chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example, 1,2,3,4-TCDD and 2,3,7,8-TCDD are structural isomers.

3.19 Laboratory Blank: See Method blank.

3.20 Laboratory Control Sample: See Ongoing precision and recovery standard (OPR).

3.21 Maximum Level (MaxL): The concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.22 Method Blank: An aliquot of reagent water, sand, sodium sulfate, or other representative matrix free of the targets of interest and interferences that is extracted and analyzed along with the samples to monitor for laboratory contamination.

3.23 Minimum Level (MinL): The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.24 MS: Mass spectrometer or mass spectrometry.

3.25 OPR: Ongoing precision and recovery standard; a laboratory blank spiked with known quantities of analytes. The OPR is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery.

3.26 PAR: Precision and recovery standard; secondary standard that is diluted and spiked to form the IPR and OPR.

3.27 PCDD: Polychlorinated dibenzo-p-dioxins.

3.28 PCDF: Polychlorinated dibenzofurans.

3.29 PFK: Perfluorokerosene; the mixture of compounds used to calibrate the exact m/z scale in the HRMS.

3.30 Recovery Standard: $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD which are added to every sample, blank, and quality control spike sample extract prior to analysis. They are used to measure the recovery of the internal standards and the cleanup standard.

3.31 Relative Percent Difference (RPD): A measure of the difference between two values normalized to one of the values. It is used to determine the accuracy of the concentration measurements of second source verification standards.

3.32 Relative Response Factor (RRF): The ratio of the response of the mass spectrometer to a known amount of an analyte relative to that of a known amount of internal standard as measured in the initial and continuing calibrations. It is used to determine instrument performance and it is used to calculate the concentration of target analytes or detection limits in samples, blanks, and quality control samples.

3.33 Signal to Noise Ratio: The ratio of the mass spectrometer response of a GC peak to the background noise signal.

3.34 Split Ratio (S): The decimal expression of the proportion of extract used from splits taken after the addition of internal standards and before the addition of recovery standards.

3.35 Window Defining Mix: A solution which contains the first and last eluting isomers of each homologue group and is used to verify that the switching times between the MID descriptors have been appropriately set.

4. Interferences

4.1 Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferences under the conditions of analysis by performing laboratory method blanks. Analysts should avoid using PVC gloves, powdered gloves, or gloves with measurable levels of phthalates.

4.2 The use of high purity reagents and solvents helps minimize interference problems. Where possible, reagents are cleaned by extraction or solvent rinse.

4.3 Interferences coextracted from the samples will vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, and polychlorinated alkyldibenzofurans that may be found at concentrations several orders of magnitude higher than the analytes of interest. Retention times of target analytes must be verified using reference standards. While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup steps to achieve lower detection limits.

5. Safety

5.1 Procedures shall be carried out in a manner that protects the health and safety of all associates.

5.2 Eye protection that satisfies ANSI Z87.1 (as per the STL Corporate Safety Manual), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated will be removed and discarded, other gloves will be cleaned immediately. VITON gloves may be worn when halogenated solvents are used for extractions or sample preparation. Nitrile gloves may be used when other solvents are handled. [Note: VITON is readily degraded by acetone; all solvents will readily pass through disposable latex rubber gloves.]

5.2.1 For the operations described herein, Nitrile clean room gloves are worn. For operations using solvents that splash, silver shield gloves are recommended. Silver shield gloves protect against breakthrough for most of the solvents used in this procedure

5.3 The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

5.3.1 Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include: benzene and methylene chloride, 2,3,7,8-TCDD and all other 2,3,7,8-substituted PCDD or PCDF isomers.

Note: The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.

5.3.2 Chemicals known to be **flammable** are: methanol, acetone, toluene, hexane, nonane, benzene, cyclohexane, and tetradecane.

5.3.3 The following materials are known to be **corrosive**: sulfuric acid, hydrochloric acid, sodium hydroxide and potassium hydroxide.

5.4 Exposure to chemicals will be maintained **as low as reasonably achievable**; therefore, unless they are known to be non-hazardous, all samples will be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5 The preparation of all standards and reagents and glassware cleaning procedures that involve solvents such as acetone, toluene, methylene chloride, and hexane will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.6 All work must be stopped in the event of a known or potential compromise to the health or safety of an associate. The situation must be reported **immediately** to a laboratory supervisor.

5.7 The effluents of sample splitters for the gas chromatograph and roughing pumps on the mass spectrometer must be vented to the laboratory hood exhaust system or must pass through an activated charcoal filter.

5.8 Training: Workers must complete the employee Corporate Safety Manual safety orientation prior to working in the laboratory.

5.9 Personal Hygiene: Thorough washing of hands and forearms is recommended after each manipulation and before breaks (coffee, lunch, and shifts).

5.10 Confinement: Work areas should be isolated and posted with signs. Glassware and tools should be segregated. Benchtops should be covered with plastic backed absorbent paper.

5.11 Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans.

5.12 Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

6. Equipment and Supplies

6.1 Sample Extraction Equipment.

Note: All glassware used in extraction and cleanup procedures is solvent rinsed before use with acetone, toluene, methylene chloride and hexane in that order, once for low resolution glassware and 2 times for high resolution glassware. Pre-extract high resolution Soxhlet apparatus with toluene for at least 4 hours. Rinse glassware with all 4 solvents once. See SOP KNOX-QA-0002, current revision, "Glassware Cleaning", for details.

6.1.1 Aqueous Sample Extraction

6.1.1.1 Multi-position separatory funnel rotator.

6.1.1.2 2000 mL separatory funnels with PFTE stopcocks and PFTE stoppers.

6.1.1.3 100 mm glass funnel with short stem.

6.1.1.4 Class A 1 mL pipettes.

6.1.1.5 1000 mL graduated cylinders.

6.1.1.6 PFTE squirt bottles, 500 mL.

6.1.1.7 Micropipetters.

6.1.1.8 Glass wool, precleaned with methylene chloride.

6.1.1.9 Buchner funnels, filter flasks, rubber stopper and GF/D filters

6.1.1.10 Vacuum source

6.1.2 Soxhlet Extraction

6.1.2.1 Dean-Stark extraction apparatus.

6.1.2.2 Heating mantles with temperature controls.

6.1.2.3 500 mL evaporative flask, round bottom.

6.1.2.4 Glass condenser, capable of sitting on top of the dean-stark extractor.

6.1.2.5 Glass wool, precleaned with methylene chloride.

6.1.2.6 Boiling beads, 6 mm glass.

6.1.2.7 PFTE boiling chips.

6.1.3 Waste Dilution

6.1.3.1 Analytical balance, capable of weighing to 0.01 g.

6.1.3.2 40 mL vial, with PFTE lined cap.

6.1.3.3 5 3/4 inch borosilicate glass pipets.

6.1.3.4 Rubber bulbs.

6.1.3.5 1 ml Class A pipette.

6.2 Sample Cleanup Equipment.

6.2.1 Acid-base cleanup

6.2.1.1 Disposable Pasteur pipets and rubber bulbs.

6.2.1.2 Graduated cylinder, 100 mL volume.

6.2.1.3 Vials, 40 mL volume, with PFTE lined caps.

6.2.1.4 Nitrogen concentration device.

6.2.2 Low pressure liquid chromatography (LPLC) cleanup

6.2.2.1 Low pressure liquid chromatography system with automated autosampler and fractionator. The system must be free of polymeric materials other than PTFE, and must be capable of gradient elution programming. The system must be capable of collecting serial fractions.

6.2.2.2 Glass columns, approximately 170mm in total length with #11 Ace® threads on both ends.

6.2.2.3 Michel-Miller PFTE 11mm adapter to match #11 Ace® threads

6.2.2.4 HPLC filters.

6.2.3 Dual column cleanup

6.2.3.1 Disposable glass columns, Corning #2142-10 drying columns or equivalent.

6.2.3.1.1 Disposable glass columns, packed with precleaned glass wool are solvent rinsed before use. The solvents used are acetone, toluene, methylene chloride and hexane (in this order).

6.2.3.2 Volumetric flask, 100 mL volume.

6.2.3.3 Disposable Pasteur pipets and rubber bulbs.

6.2.3.4 40 mL vials.

6.2.3.5 Nitrogen concentration device.

6.2.3.6 Mini vials, 1.1 mL capacity with a tapered bottom; with PFTE faced, rubber septa and screw caps.

6.2.3.7 Graduated cylinder, 100 ml.

6.2.3.8 Solvent waste collection jars.

6.2.4 Activated carbon cleanup

6.2.4.1 10 mL disposable pipet for use as the column.

6.2.4.1.1 All disposable carbon columns are solvent rinsed before use. The solvents used are acetone, toluene, methylene chloride and hexane (in this order).

6.2.4.2 Glass wool.

6.2.4.3 40 mL vials.

6.2.4.4 Nitrogen concentration device.

6.2.4.5 Mini vials, 1.1 mL capacity with a tapered bottom; with PFTE faced, rubber septa and screw caps.

6.3 Sample Concentration Equipment.

6.3.1 Macro Concentration Equipment – Rapid-Vap

6.3.1.1 Labconco Rapid-Vap concentrator

6.3.1.2 600 mL sample concentrator tubes, Labconco or equivalent.

6.3.1.3 Borosilicate 5.75 inch and 9.0 inch disposable pipettes.

6.3.1.4 Rubber bulbs.

6.3.1.5 Borosilicate 40 mL disposable vials with PFTE lined screwcaps.

6.3.2 Macro Concentration – Snyder Column

6.3.2.1 Heating mantles with temperature controls.

6.3.2.2 Three-ball macro Snyder column.

6.3.2.3 Boiling beads, 6 mm glass.

6.3.2.4 Rubber bulbs.

6.3.2.5 Nine inch borosilicate glass pipets.

6.3.2.6 40 mL vial, with PFTE lined cap.

6.3.2.7 PFTE boiling chips.

6.3.3 Micro Concentration – N-Evap

6.3.3.1 Nitrogen blowdown apparatus (N-EVAP or equivalent).

6.4 Sample Analysis Equipment.

6.4.1 Gas Chromatograph --- Shall have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and shall meet all of the performance specification in Section 10.

6.4.1.1 GC column for PCDDs/PCDFs and for isomer specificity for 2,3,7,8-TCDD --- 60m x 0.32mm ID x 0.25µm film thickness DB-5 or RTX-5 fused silica capillary column (J&W No. 123-5062, Restek No.10227 or 10227-125 IntegraGuard) or equivalent.

6.4.1.2 GC column for isomer specificity for 2,3,7,8-TCDF --- 30m x 0.32mm ID x 0.25µm film thickness DB-225 or RTX-225 fused silica capillary column (J&W No. 123-2232 or Restek No.14024) or equivalent.

6.4.2 Mass Spectrometer --- Electron impact ionization with the filament eV's optimized for best instrument sensitivity, stability and signal to noise ratio. Shall be capable of repetitively selectively monitoring 12 exact m/z's minimum at high resolution (≥10,000) during a period of approximately 1 second and shall meet all of the performance specifications in Section 10.

6.4.3 GC/MS Interface --- The mass spectrometer (MS) shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beam

6.4.4 Data System --- Capable of collecting, recording, and storing MS data.

7. Reagents and Standards

7.1 Sample Pre-Treatment

7.1.1 Hydrochloric acid (HCl), concentrated 37% wt in water (ACS), Mallinkcrodt AR Select or equivalent.

7.1.2 1M HCl - Carefully add 83ml of concentrated HCl to 917 ml of reagent water in a glass container.

7.2 Aqueous Extraction

7.2.1 Acetone, pesticide quality or equivalent.

7.2.2 Toluene, pesticide quality or equivalent.

7.2.3 Methylene chloride, pesticide quality or equivalent.

7.2.4 Hexane, pesticide quality or equivalent.

7.2.5 Nonane, pesticide quality or equivalent.

7.2.6 Tetradecane, pesticide quality or equivalent.

7.2.7 Reagent water must be produced by a Millipore DI system or equivalent, being able to produce water with 18 mega ohm resistance. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2.8 Sodium sulfate (ACS), granular anhydrous. Heated at 450 ° C for a minimum of four (4) hours. After cooling, store in a desiccator.

7.3 Soxhlet extraction

7.3.1 Acetone, pesticide quality or equivalent.

7.3.2 Toluene, pesticide quality or equivalent.

7.3.3 Methylene chloride, pesticide quality or equivalent.

7.3.4 Hexane, pesticide quality or equivalent.

7.3.5 Benzene, pesticide quality or equivalent.

7.3.6 Tetradecane, pesticide quality or equivalent.

7.3.7 Sand, prepared by extracting with methylene chloride and/or baking at 450° C for a minimum of 4 hours. After cooling store in a dessicator.

7.3.8 Sodium sulfate (ACS), granular anhydrous. Heated at 450 ° C for a minimum of four (4) hours. After cooling, store in a desiccator.

7.3.9 Dry Ice.

7.3.10 Reagent water must be produced by a Millipore DI system or equivalent, being able to produce water with 18 megaohm resistance. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.4 Waste Dilution

7.4.1 Hexane, pesticide quality or equivalent.

7.4.2 Benzene, pesticide quality or equivalent.

7.5 Acid-Base Cleanup

7.5.1 Sulfuric acid ,concentrated, ACS grade, specific gravity 1.84.

7.5.2 Potassium hydroxide, 20% aqueous. Prepare by cautiously adding, 100 grams of potassium hydroxide pellets to 400 mL of deionized water. This solution is stored at room temperature in a plastic bottle.

7.5.3 Sodium chloride, NaCl, analytical reagent, 5 percent (w/v) in reagent grade water.

7.5.4 Hexane, pesticide quality or equivalent.

7.5.5 Benzene, pesticide quality or equivalent.

7.5.6 Sodium sulfate (ACS), granular anhydrous. Heated at 450 ° C for a minimum of four (4) hours. After cooling, store in a desiccator.

7.6 Silica Gel/Alumina Column Cleanup

7.6.1 Sodium sulfate (ACS), granular anhydrous. Heated at 450 ° C for a minimum of four (4) hours. After cooling, store in a desiccator.

7.6.2 Methylene chloride pesticide quality or equivalent.

7.6.3 Hexane, pesticide quality or equivalent.

7.6.4 Acetone, pesticide quality or equivalent.

7.6.5 Toluene, pesticide quality or equivalent.

7.6.6 Silica gel, Davisil Grade 923, 100-200 mesh or equivalent. Prepare by Soxhlet extraction with methylene chloride for at least 6 hours. Air dry and activate in an aluminum foil-covered Pyrex glass container at 130°C. Store in labeled glass jars in desiccator until use.

7.6.7 Acid silica - To prepare, add 19 mL of concentrated sulfuric acid to 60 grams silica gel in a 240 mL amber-colored glass jar with a PFTE lined screw cap. Mix thoroughly by shaking until no lumps are visible, and the silica gel no longer sticks to the side of the jar.

7.6.8 Alumina, Neutral - Super I - Scientific Absorbents. Purchase and use only activated alumina. It is stored in an oven at 130° C when not in use.

7.6.8.1 Each new lot of alumina must be tested upon receipt and before use. Elute a solution containing all of the ^{13}C internal standards and native analytes through a column packed with the new lot of alumina. Collect the 5% and 60% fractions together and analyze by HRMS. Archive the 80 mL of hexane in a separate container. The target analytes and internal standard recoveries must be greater than 85% in the final fraction. If the recovery is less than 85% for any compound or internal standard, the ratios and volumes of the elution solvents must be optimized and the test repeated until all compounds meet the recovery criteria.

7.6.9 5% methylene chloride in hexane. Add 20 mL methylene chloride to 380 mL hexane. Store in an amber-colored glass bottle at room temperature until use.

7.6.10 60% methylene chloride in hexane - add 420 mL methylene chloride to 280 mL hexane. Store in an amber-colored glass bottle at room temperature until use.

7.7 Activated Carbon Cleanup

7.7.1 Thoroughly mix 5 % (by weight) active carbon AX-21 and 95 % (by weight) silica gel (Davisil Grade 923, 100-200 mesh). Activate in an oven at 130°C for 6 hours. Store in a dessicator in an amber colored bottle with a foil lined lid until use.

7.7.2 Toluene, pesticide quality or equivalent.

7.7.3 Methylene Chloride, pesticide quality or equivalent.

7.7.4 Benzene, pesticide quality or equivalent.

7.7.5 Methanol, pesticide quality or equivalent.

7.7.6 Cyclohexane, pesticide quality or equivalent.

7.7.7 Tetradecane, pesticide quality or equivalent.

7.7.8 Hexane, pesticide quality or equivalent.

7.7.9 Acetone, pesticide quality or equivalent.

7.8 7.12 Standards and Calibration Solutions: Obtained as prepared solutions from Cambridge Isotope Laboratories (CIL, Andover Massachusetts), and Wellington Laboratories (Guelph, Ontario, Canada). If the chemical purity is 97% or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at room temperature in screw-capped vials with PFTE-lined caps.

7.8.1 PAR Native Standard Stock Solution: Certified Reference Standard purchased from Cambridge Isotope Laboratories (Catalog No. EDF-7999) containing 17 native PCDD/PCDF compounds at a concentration of 40-400 ng/mL in nonane (200 µL).

7.8.2 PAR Native Standard Spiking Solution: The working spike solution is made by diluting 200 µL of the stock solution in section 7.8.1 into 40 mL of acetone. The final concentration of the spiking solution is 0.2-2.0 ng/mL. 1.0 mL of this solution is added to each IPAR sample and OPR sample. See Table 7 for a complete list of compounds and their concentrations.

7.8.3 $^{13}C_{12}$ Labeled Internal Standard Stock Solution: Certified Reference Standard purchased from Cambridge Isotope Laboratories (Catalog No. EDF-8999) containing 15 labeled compounds at a concentration of 100 ng/mL ($^{13}C_{12}$-OCDD 200 ng/mL) in nonane (500 µL).

7.8.4 $^{13}C_{12}$ Labeled Internal Standard Spiking Solution: The working spike solution is made by diluting 500 µL of the stock solution in section 7.8.3 into 50 mL of acetone. The final concentration of the spiking solution is 1.0 ng/mL ($^{13}C_{12}$-OCDD 2.0 ng/mL). 1.0 mL of this solution is added to each sample, method blank, and QC sample. See Table 13 for a complete list of compounds and their concentrations.

7.8.5 $^{37}Cl_4$ Labeled Cleanup Standard Stock Solution: Certified Reference Standard purchased from Cambridge Isotope Laboratories (Catalog No. ED-907) containing $^{37}Cl_4$-2,3,7,8-TCDD at a concentration of 50 µg/mL in nonane (1.2 mL).

7.8.6 $^{37}Cl_4$ Labeled Cleanup Standard Secondary Stock Solution: The secondary stock solution is made by diluting 0.100 mL of the stock solutions in section 7.8.5 to 1.0 mL in a volumetric flask with nonane. The final concentration of the secondary stock solution is 5.0 µg/mL.

7.8.7 $^{37}Cl_4$ Labeled Cleanup Standard Working Stock Solution: The working stock solution is made by combining 0.200 mL of the stock solutions in section 7.8.6 with 4.8 mL of nonane. The final concentration of the secondary stock solution is 200 ng/mL.

7.8.8 $^{37}Cl_4$ Labeled Cleanup Standard Spiking Solution: The spike solution is made by diluting 0.100 mL of the stock solution in section 7.8.7 to 100 mL in a volumetric graduate with hexane. The final concentration of the secondary solution is 0.20 ng/mL. 1.0 mL of this solution is added to each sample, method blank, and QC sample extract prior to cleanup. See Table 13 for a complete list of compounds and their concentrations.

7.8.9 $^{13}C_{12}$-2,3,7,8-TCDD Labeled Standard Stock Solution: Certified Reference Standard purchased from Cambridge Isotope Laboratories (Catalog No. ED-900) containing $^{13}C_{12}$-2,3,7,8-TCDD at a concentration of 50 µg/mL in nonane (1.2 mL).

7.8.10 $^{13}C_{12}$-2,3,7,8-TCDF Labeled Standard Stock Solution: Certified Reference Standard purchased from Cambridge Isotope Laboratories (Catalog No. EF-904) containing $^{13}C_{12}$-2,3,7,8-TCDF at a concentration of 50 µg/mL in nonane (1.2 mL).

7.8.11 $^{13}C_{12}$ TCDD/TCDF Labeled Standard Secondary Stock Solution: The secondary stock solution is made by diluting 0.100 mL of the stock solutions in sections 7.8.9 and 7.8.10 to 10 mL in a volumetric flask with nonane. The final concentration of the secondary stock solution is 500 ng/mL.

7.8.12 $^{13}C_{12}$ TCDD/TCDF Labeled Standard Spiking Solution: The working spike solution is made by diluting 200 µL of the stock solution in section 7.8.11 to 100 mL in a volumetric flask with acetone. The final concentration of the spiking solution is 1.0 ng/mL. 1.0 mL of this solution is added to each sample, method blank, and QC sample extract that are extracted for TCDD and/or TCDF analysis only.

7.8.13 $^{13}C_{12}$ Labeled Recovery Standard Stock Solution: Certified Reference Standard purchased from Cambridge Isotope Laboratories (Catalog No. ED-911) containing $^{13}C_{12}$-1,2,3,4-TCDD at a concentration of 50 µg/mL in nonane (1.2 mL) and (Catalog No. ED-996) containing $^{13}C_{12}$-1,2,3,7,8,9-HxCDD at a concentration of 50 µg/mL in 80% nonane/20% toluene (1.2 mL).

7.8.14 $^{13}C_{12}$ Labeled Recovery Standard Secondary Stock Solution: The secondary stock solution is made by diluting 1.0 mL of the stock solutions in section 7.8.13 to 10 mL

in a volumetric flask with nonane. The final concentration of the secondary stock solution is 5.0 µg/mL.

7.8.15 $^{13}C_{12}$ Labeled Recovery Standard Spiking Solution: The working spike solution is made by diluting 200 µL of the stock solution in section 7.8.14 to 10 mL in a volumetric flask with nonane. The final concentration of the spiking solution is 0.1 µg/mL. 20 µL of this solution is added to each sample, method blank, and QC sample extract.

7.8.16 Initial Calibration Standards: CS1-CS5. Certified Reference Standard purchased from Cambridge Isotope Laboratories (Catalog No. EDF-9999). See Table 3 for a complete list of compounds and their concentrations. The standards are used as received after being sonicated and transferred to 1.0 mL amber glass vials with PFTE lined caps.

7.8.17 Continuing Calibration Standard: The same as Initial Calibration Standard CS3 above. Certified Reference Standard purchased from Cambridge Isotope Laboratories (Catalog No. EDF-9999-3). The standard is used as received after being sonicated and transferred to a 1.0 mL amber glass vial with a PFTE lined cap.

Note: A version of the Continuing Calibration Standard is available which includes the Window Defining Mix and the Isomer Specificity Mix. This standard may be used as both the Continuing Calibration Standard and the DB/Rtx-5 GC Window Defining Mix/Column Performance Check Solution. Cambridge Isotope Laboratories (Catalog No. EDF-4141 - 0.2 mL ampule)

7.8.18 Window Defining Mixture: Cambridge Isotope Laboratories (Catalog No. ED-1731-A and ED-1732-A). See Table 4 for a complete list of compounds. The solution is prepared with nonane or tetradecane as the solvent. This standard is used for qualitative purposes only and is not considered quantitative. (note: this standard may be combined with the Column Performance Solution Mixture)

7.8.19 Column Performance Solution Mixture: Cambridge Isotope Laboratories (Catalog No. ED-908). See Table 4 for a complete list of compounds. The solution is prepared with nonane or tetradecane as the solvent. This standard is used for qualitative purposes only and is not considered quantitative. (Note: This mixture does not contain 1,2,3,9-TCDD, which must be added as a separate solution. This standard may be combined with the Window Defining Mixture)

7.8.20 1,2,3,9-TCDD Standard Stock Solution: Cambridge Isotope Laboratories (Catalog No. ED-948). The solution is prepared with nonane or tetradecane as the solvent. This standard is used for qualitative purposes only and is not considered quantitative.

7.8.21 Initial Calibration Verification Standard: Wellington Laboratories (Catalog No. EPA-1613-CS3). The standard is used as received after being sonicated and transferred to a 1.0 mL amber glass vial with a PFTE lined cap.

7.8.22 Stability of Solutions --- Standard solutions used for quantitative purposes should be analyzed periodically, and should be assayed against reference standards before further use.

7.9 Perfluorokerosene (PFK) is used in neat form to tune and calibrate the mass spectrometer. Fluka (Catalog No. - 77275) has been found to be superior to other sources of PFK.

8. Sample Collection, Preservation and Storage

8.1 Collect samples in amber glass containers following conventional sampling practices. Maintain samples in the dark at 0-4°C from the time of collection until receipt in the laboratory. If residual chlorine is present in aqueous samples, add 80 mg sodium thiosulfate per liter of water. If sample pH is greater than 9, adjust to pH 7-9 with sulfuric acid.

8.2 Store aqueous samples in the dark at 0-4°C. Store solid, semi-solid, multi-phase, and tissue samples in the dark at <-10°C.

8.3 There are no demonstrated maximum holding times associated with PCDDs/PCDFs in aqueous, solid, semi-solid, tissue, or other sample matrices. If stored in the dark at 0-4°C and preserved as given above (if required), aqueous samples may be stored for up to one year. Similarly, if stored in the dark at <-10°C, solid, semi-solid, multi-phase, and tissue samples may be stored for up to one year.

8.4 Extracts should be stored in the dark at room temperature in amber or clear glass vials prior to analysis.

9. Quality Control

9.1 Initial precision and recovery (IPR) samples are analyzed to demonstrate the ability to generate acceptable precision and accuracy.

9.1.1 For aqueous samples, extract, concentrate, and analyze four 1-L aliquots of reagent water spiked with labeled internal standards and the precision and recovery standard according to the procedures in section 11. For non-aqueous samples, extract, concentrate, and analyze four aliquots of sand or sodium sulfate spiked with labeled internal standards and the precision and recovery standard according to the procedures in section 11.

9.1.2 Using the results of the set of four analyses, compute the average concentration (X) of the extracts in ng/mL and the standard deviation of the concentration (s) in ng/mL for each compound.

9.1.3 For each compound, compare s and X with the corresponding limits for initial precision and recovery in Table 10. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, compare s and X with the corresponding limits for initial precision and recovery in Table 12. If s and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however,

any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound. Correct the problem and repeat the test.

9.2 Internal standards are spiked into all samples, blanks, and laboratory control samples to assess method performance on the sample matrix. The recovery of each labeled internal standard must be within the limits in Table 13 when all 2,3,7,8-substituted PCDDs/PCDFs are determined, and within the limits in Table 14 when only 2,3,7,8-TCDD and 2,3,7,8-TCDF are determined.

9.3 A laboratory method blank must be run along with each analytical batch of 20 or fewer samples. The method blank must not contain any of the compounds of interest at a concentration above the minimum level.

9.4 An ongoing precision and recovery (OPR) sample is analyzed along with each analytical batch of 20 or fewer samples. OPR spike components, concentrations, and control limits are given in Table 10. If only 2,3,7,8-TCDD and 2,3,7,8-TCDF are to be determined, the limits for ongoing precision and recovery are listed in Table 12.

9.5 Corrective action: If the method blank or OPR sample fails to meet the acceptance criteria, the Project Manager is notified and the entire sample batch is re-extracted. If there is insufficient sample volume remaining for re-extraction, the client is contacted for information about the availability of additional sample volume. If there is no additional sample available, the original sample data is flagged and reported. A nonconformance memo is initiated describing the problem and corrective action. The problem and corrective action is documented in the project narrative.

10. Calibration and Standardization

10.1 Two types of calibration procedures are required. One type, initial calibration, is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by the results of continuing calibration procedures described below. The other type, continuing calibration, consists of analyzing the column performance check solution and a calibration solution (CS3). No samples are to be analyzed until acceptable calibration as described in sections 10.2 and 10.2.9.1 is demonstrated and documented.

10.2 Initial Calibration

10.2.1 Prepare multi-level calibration standards containing the compounds and concentrations as specified in Table 3. Calibration standards should be stored at room temperature and preferably in amber vials. Calibration standard solutions have an expiration date of ten (10) years from date of receipt unless otherwise specified by the manufacturer/supplier.

10.2.2 Establish operating parameters for the GC/MS system (suggested operating conditions are displayed in Figure 1 and Figure 2) necessary to meet the relative retention times for the PCDDs/PCDFs listed in Table 8.

10.2.3 By using a PFK molecular leak, tune the instrument to meet the minimum resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or any other reference signal close to the m/z 303.9016 (from TCDF). By using peak matching conditions and the aforementioned PFK reference peak, verify that the exact mass of m/z 380.9760 (PFK) is within 5 ppm of the required value. Document that the resolving power at reduced accelerating voltage of m/z 380.9760 is greater than 10,000 (10 percent valley).

10.2.4 Analyze 2µL of the Window Defining Mixture and set the switchpoints for the MID descriptors. The switchpoints must be set to encompass the retention time window of each congener group.

10.2.5 If the initial calibration is being performed on the DB-5 or RTX-5 column, analyze 2µL of the Column Performance solution or Mixture Solution. The chromatographic peak separation between 2,3,7,8-TCDD and the closest eluting non-2,3,7,8-TCDD isomer must be resolved with a % Valley of ≤ 25, where

$$\% \text{ Valley} = \frac{\text{baseline to valley height of closest eluting isomer}}{\text{peak height of 2,3,7,8 - TCDD}} \times 100$$

If the initial calibration is being performed on the DB-225 or RTX-225 column, analyze 2µL of the TCDF Column Performance solution. The chromatographic peak separation between 2,3,7,8-TCDF and the closest eluting non-2,3,7,8-TCDF isomer must be resolved with a % Valley of ≤ 25, where

$$\% \text{ Valley} = \frac{\text{baseline to valley height of closest eluting isomer}}{\text{peak height of 2,3,7,8 - TCDF}} \times 100$$

10.2.6 Analyze 2µL of each of the five calibration standards and calculate the RRF of each analyte vs. the appropriate internal standard listed in Table 8 using the following equation;

$$RRF = \frac{As \times Cis}{Ais \times Cs}$$

where:

As = sum of the areas of the quantitation ions of the compound of interest
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Cis = concentration of the appropriate internal standard
Cs = concentration of the compound of interest

10.2.7 Calculate the mean relative response factor and the standard deviation of the relative response factors for each calibration standard solution.

10.2.8 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met before sample analyses are performed. If acceptable initial

calibration is not achieved, identify the root cause, perform corrective action, and repeat the initial calibration. If the root cause can be traced to problems with an individual analysis within the calibration series, repeat the individual analysis and recalculate the percent relative standard deviation. If the calibration is acceptable, document the problem and proceed; otherwise repeat the initial calibration.

10.2.8.1 The percent relative standard deviation (RSD) for the mean relative response factors from the unlabeled native analytes, except 1,2,3,7,8,9-HxCDD and OCDF must not exceed ± 20 percent, and those for 1,2,3,7,8,9-HxCDD, OCDF, and the labeled internal standards must not exceed ± 35 percent.

10.2.8.2 The peaks representing the PCDDs/PCDFs and labeled compounds in the calibration standards must have signal-to-noise ratios (S/N) ≥ 10.

10.2.8.3 The ion abundance ratios must be within the specified control limits in Table 6.

10.2.8.4 The absolute retention time of $^{13}C_{12}$-1234-TCDD must exceed 25.0 minutes on the DB/Rtx-5 column and 15.0 minutes on the DB/Rtx-225 column.

10.2.9 Analyze 2µL of the Initial Calibration Verification (ICV) Standard in section 7.8.21. Calculate the concentration of the ICV using the RRF's from the CS3 standard analyzed in section 10.2.6. Calculate the percent difference (%D) between the expected and the calculated ICV concentration using the following formula.

$$\%D = \frac{(C_{Exp} - C_{Calc})}{C_{Exp}} \times 100$$

Where:

C_{Exp} = The expected concentration of the ICV Standard.
C_{Calc} = The calculated concentration of the ICV Standard.

10.2.9.1 The general criteria for percent difference acceptance limits is less than or equal to ±35% for all native and labeled compounds. The warning limits for percent difference is ±35 - 55%.

10.2.9.2 All data associated with compounds with percent differences in the warning limits must be reviewed before acceptance.

10.2.9.3 All data associated with compounds with percent differences outside the warning limits shall be documented as an NCM. Corrective action must be taken and may include the following

- Reanalyze the ICV Standard
- Replace and reanalyze the ICV Standard
- Evaluate the instrument performance
- Evaluate the Initial Calibration Standards

10.3 Continuing Calibration

10.3.1 Continuing calibration is performed at the beginning of a 12 hour period after successful mass resolution and GC resolution performance checks.

10.3.2 Document the mass resolution performance as specified in section 10.2.3. The mass resolution checks must be performed at the beginning and at the end of each 12-hour shift.

10.3.3 Analyze 2µL of the Window Defining Mixture and or Column Performance Solution Mixture under the same instrument conditions used to perform the initial calibration. Determine and document acceptable column performance as described in section 10.2.4 and 10.2.5.

10.3.4 Analyze 2µL of the Daily Calibration Standard Solution (CS3). Calculate the concentrations using the formulas in section 12.2.

Note: The combined Continuing Calibration Standard/Window Defining Mix/Column Performance Solution specified in section 7.8.17 may be used in section 10.3.2, 10.3.4, and 10.3.6.

10.3.5 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met before sample analyses are performed. If acceptable continuing calibration is not achieved, identify the root cause, perform corrective action, and repeat the daily calibration.

10.3.5.1 The measured concentration for each compound must be within the specified control limits in Table 9 when all PCDDs/PCDFs are being determined or Table 11 if only 2,3,7,8-TCDD and 2,3,7,8-TCDF are being determined.

10.3.5.2 The relative retention times of PCDDs/PCDFs and labeled compounds in the standard must be within the limits in Table 8.

10.3.5.3 The peaks representing the PCDDs/PCDFs and labeled compounds in the calibration standard must have signal-to-noise ratios (S/N) ≥ 10.

10.3.5.4 The ion abundance ratios must be within the specified control limits in Table 6.

10.3.6 Daily calibration must be performed every 12 hours of instrument operation. The 12 hour shift begins with the documentation of the mass resolution followed by the injection of the Window Defining Mixture or Column Performance Solution Mixture and the Daily Calibration Standard. The mass resolution documentation must also be performed at the end of the 12 hour shift. If the lab is operating consecutive 12 hour shifts, the mass resolution check from the end of the previous period can be used for the beginning of the next period.

11. Procedure

11.1 One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variations in sample matrix, radioactivity,

chemistry, sample size, or other parameters. Any variations in the procedure, except those specified by project specific instructions, shall be completely documented using a Nonconformance Memo and approved by a Technical Specialist, Project Manager, and QA Manager. If contractually required, the client shall be notified.

Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.2 Sample Pretreatment

11.2.1 Tissue Samples

11.2.1.1 If the sample matrix is tissue and has not been homogenized prior to sample receipt, the entire sample is blended to provide a homogeneous sample.

11.2.1.2 Cut tissue into pieces of a uniform size (approximately 1 inch square). Homogenize the tissue sample in a laboratory blender.

11.2.1.3 Weigh out 10 grams of the homogenized tissue sample. Add the 10 g sample along with 20 g of sodium sulfate to a laboratory blender. Blend the tissue/sodium sulfate mixture, while adding dry ice as necessary, to achieve a powder like consistency.

11.2.1.4 Record the sample and weight on the sample prep sheet or in a logbook.

11.2.2 Fly Ash Samples

11.2.2.1 Weigh 10 g of the fly ash sample (+/- 0.05 grams weighed to two significant figures) and transfer to a 240 mL glass jar. Record the sample and weight on the sample prep sheet.

11.2.2.2 Add 1.0 mL of the internal standard spiking solution (see section 7.8.4) to the sample. Record the standard solution ID and volume spiked on the sample prep sheet. Initial and date the entry. Add 150 mL of 1 M HCl to the sample. Seal the jar with a PFTE lined screw cap and shake for 3 hours at room temperature.

11.2.2.3 Rinse a glass fiber filter with reagent water, and filter the sample through the filter paper, placed in a Buchner funnel, into a 1 L flask. Rinse the sample bottle twice with small amounts of reagent water, making sure that all particulate matter is transferred onto the glass fiber filter. Wash the fly ash cake with approximately 500 mL organic-free reagent water.

11.2.2.4 Extract the sample and glass fiber filter by Dean-Stark Soxhlet extraction in section 11.4.

11.3 Aqueous Sample Extraction

11.3.1 Remove the samples from the refrigerator several hours before extraction and allow them to come to room temperature before measuring the volume or performing the extraction.

11.3.2 Refer to Knoxville SOP, KNOX-QA-0002, current revision, for information on glassware cleaning procedures for extraction glassware. Visually inspect all glassware prior to use for scratches or cracks. Retire and replace any glassware found to be damaged.

11.3.3 Place separatory funnels, one for each sample, the method blank, and the OPR, in the positions in the rotary extractor.

11.3.4 Place a 600 mL concentration tube directly beneath each separatory funnel in the tube holder.

11.3.5 Plug a glass funnel with glass wool and pour in some sodium sulfate (about 1 to 2 inches from the top). Rinse the sodium sulfate with methylene chloride. After the funnel stops dripping, place the funnel on top of the concentrator tube.

11.3.6 Inspect the sample for solids or biphasic sample characteristics. If either condition exists, document the observation on the sample tracking sheet and consult the project manager for further instructions (see 11.3.6.1 – 11.3.6.4.4 below). If solids are not observed in the sample, mark the level of the sample on the sample bottle in order to measure the volume later and carefully add the sample to the separatory funnel, taking care not to spill any sample. Using a 1000 mL graduated cylinder measure out 1000 mL of reagent water and add to the separatory funnels marked for the method blank and OPR.

11.3.6.1 If the sample exhibits biphasic characteristics, the sample can either be mixed and extracted as an aqueous sample or the phases can be separated and extracted individually. The decision as to which approach to use should be made in consultation with the Project Manager and the Client. Document the decision process as well as the characteristics and relative volumes of each sample phases.

11.3.6.2 If visible solids are present, determine the percent solids in the sample. Add 10 mL of the well shaken sample to an pre-weighed aluminum weighing dish. Weigh the dish to three significant figures. Dry overnight in an oven at 105°C. Reweigh the dish and calculate the percent solids using the following equation.

$$\%solids = \frac{\text{weight of dish plus sample after drying} - \text{weight of dish}}{\text{weight of dish plus sample before drying} - \text{weight of dish}} \times 100$$

11.3.6.3 If the sample contains greater than one percent suspended solids, a sample aliquot sufficient to provide 10 grams of dry solids is used and the sample is extracted following the procedure in section 11.4.

11.3.6.4 If the sample contains less than one percent suspended solids, the sample is filtered through a Buchner funnel with a 2.7 um glass fiber filter with the following procedure.

11.3.6.4.1 Assemble a Buchner funnel with a rubber stopper on top of a clean filter flask. Insert a 2.7 um glass fiber filter into the funnel. Apply vacuum to the flask, mark the level of the sample on the sample bottle in order to measure the volume later and carefully add the sample to the Buchner funnel, swirling the sample remaining in the bottle to suspend any particles.

11.3.6.4.2 Rinse the sample bottle twice with approximately 10 mL portions of reagent water to transfer any remaining particles onto the filter. Rinse any particles off the sides of the Buchner funnel with small quantities of reagent water.

11.3.6.4.3 Add the filtrate to a separatory funnel and continue extraction in section 11.3.7.

11.3.6.4.4 Extract particulates on the filter and the filter itself following the procedure in section 11.4. **Do not add internal standards to this portion of the sample, only add internal standards to the aqueous portion of the sample!** The resulting extract is combined with the extract of the aqueous portion during the macro concentration step in section 11.6.

11.3.7 Using a Class A 1 mL volumetric pipet, add 1 mL of the ^{13}C labeled internal standard spiking solution, as specified in section 7.8.4, to each sample, the method blank, and the OPR. Record the amount of spike used and the spike solution number in the standards logbook and on the benchsheet.

11.3.8 Using a Class A 1 mL volumetric pipet, add 1 mL of the PAR native spiking solution, as specified in section 7.8.2, to the designated OPR sample. Record the amount of spike used and the spike solution number in the standards logbook and on the benchsheet.

11.3.9 Add 60 mL of methylene chloride to the sample bottle and shake. Then add the methylene chloride to the separatory funnel. Add 60 mL of methylene chloride to the method blank and OPR as well.

11.3.10 Securing the separatory funnel with the rotator retaining straps and rotate for 2 minutes.

CAUTION: Care should be used while performing this operation. Vent the separatory funnel frequently. Goggles may be worn when performing this procedure.

11.3.11 Allow the water and the methylene chloride to separate for 10 minutes. If it is not separated after 10 minutes, try to break up the emulsion by gently swirling the sample or tilting the separatory funnel on its side.

11.3.12 Drain the methylene chloride from the separatory funnel into the glass funnel that is filled with sodium sulfate, allowing the extract to drip into the concentrator tube. Be careful not to allow water to escape the separatory funnel or the sodium sulfate will harden and block the flow of the extract. When an emulsion is present, do not drain the emulsion until the third methylene chloride shake has been completed.

11.3.13 Repeat steps 11.3.9 through 11.3.12 two more times.

11.3.14 After the third methylene chloride portion has filtered through the sodium sulfate, rinse the funnel with approximately 40 mL of methylene chloride.

11.3.15 Remove the separatory funnel from the hood and pour the extracted water into the extracted waters waste carboy.

11.3.16 Fill the empty sample bottle to the marked level with tap water. Pour the tap water into a 1000 mL graduated cylinder. Record the volume of sample used on the benchsheet.

11.3.17 Proceed to Macro Extract Concentration by Rapid-Vap in section 11.5.

11.4 Soxhlet Extraction

11.4.1 Prepare and label the required number of Soxhlet systems.

NOTE: The Dean-Stark apparatus is installed between the Soxhlet body and the condenser when the components are assembled.

11.4.1.1 The Soxhlet is prepared by cleaning and rinsing per section 6.1. For blank and LCS samples, include a glass fiber extraction thimble with sand or sodium sulfate for the preclean.

11.4.2 Transfer 10 grams of the solid sample (wet weight) into a precleaned glass fiber extraction thimble or glass fiber filter paper and put the thimble or filter inside the Soxhlet (+/- 0.05 grams weighed to two significant figures). If tissue samples are being extracted, add the entire sample and sodium sulfate mixture prepared in section 11.2.1.3. Record the sample and weight on the sample prep sheet. Initial and date the entry.

11.4.2.1 If the matrix is tissue samples, sodium sulfate and dry ice are used for the blank and OPR. Transfer 20 grams of the sodium sulfate and several small chips of dry ice into an extraction thimble.

11.4.3 Pour approximately 350 mL toluene into a 500 mL round bottom flask. Place the flask in the heating mantle. Add 10-15 boiling beads and several PFTE boiling chips.

11.4.4 Place the extraction thimble in the glass Soxhlet extractor.

11.4.5 Assemble the Soxhlet system and secure to the lab supports.

11.4.6 Spike each sample with 1.0 ml of the internal standard spiking solution (see section 7.8.4) and add a small amount of glass wool if needed to the top of the extraction thimble. Record the standard solution ID and volume spiked on the sample prep sheet. Initial and date the entry.

Note: Omit this step if internal standards have been previously added to fly ash samples during acid pre-treatment (section 11.2.2.2).

11.4.6.1 Spike the OPR with 1.0 ml of the PAR native spiking solutions (see section 7.8.2) prior to adding the glass wool. Record the standard solution ID and volume spiked on the sample prep sheet. Initial and date the entry.

11.4.7 Adjust the temperature of the heating mantle to bring the toluene in the round bottom flask to a rolling boil. There should be a steady drip from the condensers so that the solvent should completely cycle at least 5 times an hour.

11.4.8 Soxhlet extract the sample in the above manner for a minimum of 16 hours. At the end of the extraction period turn off the heating mantles.

11.4.9 Remove the condensers and empty the Soxhlet extractor chamber, then remove the Soxhlet extractor from the 500 mL round bottom flask.

11.4.10 Add several (2-3) fresh boiling chips to the flasks. Insert a three-ball macro Snyder column into the top of the 500 mL round flask.

11.4.11 Place the 500 mL flask back into the heating mantle and reduce the extract volume to approximately 10-15 mL.

11.4.12 Transfer the extract into a 40 mL vial containing 100 uL of tetradecane, rinsing the 500 mL flask 3 times with 3 mL of toluene. Add the rinsings to the 40 mL vial.

11.4.13 Place the 40 mL vials into the nitrogen concentration device and reduce the volume to near dryness. Add 4 mL of hexane and swirl the vial. Reduce the volume of hexane to near dryness again to complete the solvent exchange. If the sample exhibits poor solubility in hexane, add approximately 1 mL of benzene with a pipet to the vial to aid in dissolving the residue. Adjust the final volume of the extract with hexane to 12 mL for acid-base cleanup or 2 mL for column cleanup. Proceed to sample cleanup in section 11.7.

11.5 Waste Dilution

11.5.1 Organic wastes, oil, solids that will dissolve in solvent, and non-aqueous sludge samples may be prepared by the waste dilution technique.

11.5.2 Add an appropriate amount of sample (e.g., 1.0 g) to a 40 mL VOA vial. Add 1.0 ml of the internal standard spiking solution (see section 7.8.4) to the sample. Record the spike solution number and the volume spiked on the sample prep sheet. Initial and date the entry. Add hexane to bring the volume to 12 mL. If the sample exhibits poor solubility in hexane, add approximately 1 mL of benzene with a pipet to the vial to aid in dissolving the sample.

11.5.3 Prepare a method blank and OPR sample by adding 12 mL of hexane to a 40 mL VOA vial. Add 1.0 ml of the PAR native spiking solutions (see section 7.8.2) to the OPR sample. Record the spike solution identification number and the volume spiked on the sample prep sheet. Initial and date the entry.

11.5.4 Record the weights and volumes used on the laboratory bench sheets.

11.5.5 Proceed to sample extract cleanup in section 11.7.

11.6 Macro Extract Concentration by Rapid-Vap

11.6.1 Preheat the unit to the appropriate temperature for the solvent used in the extraction.

11.6.2 Set the operating parameters on the programmer. For example, if the there is 300 ml of a methylene chloride extract, the following parameters may be used:

Temperature	35°C
Vortex Speed	50%, to be increased at a later time
Nitrogen	9 psi
Timer Set	40 minutes

11.6.3 Place 600 ml concentrator tubes containing the extract in the Rapid-Vap. Begin concentrating the extract, adjust the vortex speed for the proper rate of concentration.

11.6.4 When the extract has been concentrated to less than 20 mL, add approximately 60 mL of hexane. Concentrate the extract to a final volume of approximately 2 ml. Shut off the nitrogen flow and turn off the Rapid-Vap or remove the 600 mL concentrator tube to prevent further concentration.

11.6.5 Transfer the extract to a 40 ml vial with a 9" disposable pipet, rinsing the sample tube three times with 3 ml of hexane. Reduce the volume in the 40 mL vial using the N-Evap to approximately 2 ml and proceed to extract cleanup in section 11.7.

11.7 Sample Extract Cleanup

11.7.1 Add 1.0 mL of the ^{37}Cl-,2,3,7,8-TCDD cleanup standard (see section 7.8.8) to each sample extract as well as the method blank and OPR sample extracts.

11.7.2 Acid-Base Cleanup

The acid-base cleanup is employed when sample extracts are colored and/or oily in appearance, or if specified by the client or project manager.

11.7.2.1 Bring the extract volume up to 12 mL with hexane in a 40 ml vial.

NOTE: If the extracts are from fish tissue, omit sections 11.7.2.2 and 11.7.2.3.

11.7.2.2 Wash the extract by adding 10 mL of 20% aqueous potassium hydroxide to the vial and gently shaking for 20 seconds. If an emulsion begins to form, discontinue shaking. Vent the vial frequently while shaking. Let the vial stand for 10 minutes or until the emulsion settles and remove the aqueous layer with a glass pipet. Repeat the base washing until no color is visible in the base layer (perform a maximum of four base washings).

11.7.2.3 Add 10 mL of 5% (w/v) aqueous sodium chloride to the vial and gently shake for 20 seconds. If an emulsion forms, discontinue shaking. Vent the vial frequently

while shaking. Let the vial stand for 10 minutes and remove the aqueous layer with a glass pipet.

11.7.2.4 Slowly add 15 mL of concentrated sulfuric acid to the vial and shake for 30 seconds. If an emulsion forms, discontinue shaking. Vent the vial frequently while shaking. Let the vial stand for a minimum of 10 minutes and remove the aqueous layer with a glass pipet. Repeat the acid washing until no color is visible in the acid layer (perform a maximum of four acid washings).

11.7.2.5 Add 10 mL 5% (w/v) aqueous sodium chloride to the vial and gently shake for 20 seconds. Vent the vial frequently while shaking. Let the vial stand for 10 minutes (allowing the emulsion to settle when applicable) and remove the aqueous layer with a glass pipet. Dry the hexane extract by adding 1 to 2 grams of sodium sulfate and swirling the vial.

11.7.2.6 Reduce the extract volume to approximately 2 ml.

11.7.2.7 Proceed to section 11.7.3, silica gel/alumina column cleanup.

11.7.3 Silica gel/alumina column cleanup

Silica gel/alumina column cleanup is employed when sample extracts are clear or after other cleanup techniques have been employed. If treated drinking water samples are being analyzed, further cleanup may not be necessary.

11.7.3.1 Prepare 2 columns for each sample as specified in section 6.2.3.1.

11.7.3.2 Place a ball of glass wool in the bottom of each column.

11.7.3.3 Attach the columns, prepared as described in section 6.2.3.1, to the lab supports in the hood so that the silica gel column is above the alumina column and the lower tip of the silica gel column can be inserted into the top of the alumina column.

11.7.3.4 Pack the silica gel column with the following layers. Add the column packings in the order listed (from bottom to top) while tapping the column to settle the contents to prevent channeling.

11.7.3.4.1 3 cm layer of silica gel

11.7.3.4.2 6 cm layer of acid silica gel.

11.7.3.4.3 1 cm layer of sodium sulfate.

11.7.3.5 Pack the alumina column with the following layers. Add the column packings in the order listed (from bottom to top) while tapping the column to settle the contents to prevent channeling.

11.7.3.5.1 2 cm layer of sodium sulfate.

11.7.3.5.2 8 cm layer of neutral alumina

11.7.3.5.3 2 cm layer of sodium sulfate

11.7.3.6 Place a 125 ml clear glass jar, labeled with the sample ID, under each set of columns to catch the solvent wastes as they filter through the columns.

11.7.3.7 Pour 80 mL of hexane into a volumetric flask and save for later use in the procedure (one volumetric flask for each set of columns).

11.7.3.8 Wet both columns with 20 ml of hexane to remove any air bubbles . Discard these solvents into the solvent waste. Take care not to let the columns drip dry at any time during this procedure.

11.7.3.9 Insert the bottom tip of the silica column into the top of the alumina column.

11.7.3.10 Just before the level of hexane reaches the top of the silica gel layer, transfer the sample extract into the top of the silica gel column. Rinse the vial 3 times with 2 mL portions of hexane and add these rinses to the silica gel column.

11.7.3.11 Just before the sample volume reaches the top of the silica gel, pour the 80 mL of hexane into the top of the silica gel column and allow this to drip through the alumina column and into the collection jar. When the hexane has dripped through the silica gel column, completely remove this column leaving only the alumina column. At this point, the sample is partially purified and the analytes should be bound to the alumina.

11.7.3.12 Just before the hexane from the silica gel column reaches the top of the sodium sulfate in the alumina column, add 8 mL of 5 % methylene chloride into the top of the alumina column. Immediately slip a 40 mL vial underneath the alumina column to begin catching the eluants.

11.7.3.13 As the 5% methylene chloride reaches the top of the sodium sulfate, add 28 mL of 60% methylene chloride into the alumina column and allow this to drip into the same respective 40 mL vials. Save this portion.

11.7.3.14 Place vials containing the extract in the nitrogen concentration apparatus and reduce the solvent volume to approximately 0.3 ml.

11.7.3.15 If activated carbon cleanup is required, proceed to section 11.7.4. If no further cleanup is necessary, proceed to section 11.7.6.

11.7.4 Activated carbon cleanup

Carbon column cleanups should be performed when site history indicates carbon columns are necessary for removal of interferences. Carbon columns should also be run if, when running the extracts through dual columns, it is noticed that the acid silica layer becomes colored along the entire length of the acid silica.

11.7.4.1 Prepare a 10 mL disposable pipette by cutting off the tapered end to achieve a 12-cm column. Insert a glass-wool plug of about 1 cm in length at one end and pack

the column with 4.1 cm of the of the AX-21 Carbon/Silica Gel mixture. Hold the packing by inserting an additional glass wool plug, again about 1 cm in length, in the other end.

11.7.4.2 Pre-elute the column with 5 mL of cyclohexane/methylene chloride (50:50 v/v). Turn the column over and pre-elute in the opposite direction with another 5 mL of cyclohexane/methylene chloride (50:50 v:v).

11.7.4.3 When the solvent reaches the glass wool, add the sample extract. Rinse the sample vial 2 times with 2 ml of 50/50 cyclohexane/methylene chloride. Add these rinses to the column. Elute the column with the following sequence of solvents:

11.7.4.3.1 6 mL of cyclohexane methylene chloride (50:50 v/v).

11.7.4.3.2 5 mL of methylene chloride/methanol/benzene (75:20:5 v/v).

11.7.4.4 Allow the 75:20:5 methylene chloride/methanol/benzene to drain completely. Turn the column over and in the direction of reverse flow elute the PCDD/ PCDF fraction with 25 mL toluene into a 40 mL vial containing 100 uL of tetradecane.

11.7.4.5 Place the vial containing the eluate in the nitrogen concentration apparatus and reduce the solvent volume to near dryness. Add 4 mL of hexane and swirl the vial. Reduce the volume of hexane to near dryness again to complete the solvent exchange. Adjust the final volume of the extract with hexane to 2 mL.

11.7.4.6 Proceed to silica gel/alumina column cleanup section 11.7.3.

11.7.5 Low-Pressure Liquid Chromatography (LPLC) Cleanup.

11.7.5.1 Check the system to assure that the appropriate parts of the LPLC system are on and are in the right operating mode.

11.7.5.1.1 The autosampler and the gradient pump both need to be on and in the auto position. This allows them to be operated by the Foxy 200 fraction collector.

11.7.5.1.2 The UV detector can be left on standby.

11.7.5.1.3 The solvent bottles and the waste collection bottles are located in back of the autosampler. Confirm that the bottles contain sufficient solvents to run the amount of extracts required. Confirm that there is enough room in the waste solvent bottle to hold all the solvent it will collect.

11.7.5.1.4 All programming and functions take place and are controlled by the Foxy 200 fraction collector. Four programs are shown on the menu; A,B,C, or D. Program B is designated for the dioxin/furan clean-up procedure. Push softkey B to load program B into the Foxy 200.

11.7.5.1.5 Several options come up when program B is loaded, it can be quick-viewed, edited, ready, or save as. The saved version is the most updated version so no

programming should have to be done and the program has already been saved. To set up the system for the correct number extracts to be run, go into the edit screen. (Push softkey C to go into the edit program.)

11.7.5.1.6 Push soft key D to go the page 2 of the edit screen and then choose the restart option or soft key B. Choose soft key C, which is the timed option.

11.7.5.1.7 Enter a value for how many collections the Foxy 200 will make before starting to collect for the next extract. A 10 second flush is set at the end of each program to make sure the drop collector is clean. Push the number 1 and then soft key "enter" to proceed.

11.7.5.1.8 Choose soft key A, which is the choice of starting the collection with the next tube. The screen used to specify how many columns you will run is now displayed. Enter the number of runs, or columns to run and then push soft key "enter". The system returns to the beginning of page 2.

11.7.5.1.9 The columns need to be prepared next. Prepare one column for each extract that needs to go through column clean-up. The columns are glass, approximately 170mm in total length with #11 ace threads on both ends. One end of the column gets a glass wool plug placed in it several cm long and a Michel-Miller PFTE 11mm adapter attached to the #11 ace threads.

11.7.5.1.10 Once the glass wool is in place, the column is filled in the following order: 6g of alumina, 2g of silica gel, 4g of acidic silica gel, and a small layer of sodium sulfate on top. Use another piece of glass wool to hold the packings in place and attach another 11mm adapter to the column.

11.7.5.1.11 Place the columns on the SQ 1600 separation solutions rack. Check the number shown on the front of the unit in the "column in use" screen. Place the first column in the spot that corresponds to that number. 1-8 is found on the left side of the SQ 1600 and 9-16 are on the right. The numbers can found near the bottom of the unit underneath the outlet lines.

11.7.5.1.12 Attach the tubing coming from the top of the SQ 1600 into the top of the column and the one from the bottom into the bottom of the column. When setting up multiple columns, check to determine that no tubing is cross-connected to the wrong column.

11.7.5.1.13 Transfer the extracts into 15ml test tubes (16mm X 100mm) that have been rinsed and have been marked at 12ml. After completely transferring the extracts with hexane bring the volume up to 12ml with hexane. Transfer the sample label to the test tube.

11.7.5.1.14 Place the test tube with the extract directly underneath the needle on the autosampler. Follow each extract on the autosampler with a test tube with 12ml

of hexane in it. That is to make sure all the extract is loaded onto the column and to rinse the autosampler so that cross contamination is minimized.

11.7.5.1.15 Set up the correct number of 40ml vials on top of the Foxy 200 fraction collector. For our D/F clean-up 2 vials will need to be labeled with the correct ID and a third vial will need to be placed after the first 2 to catch the 10 second rinse of the drop former after the clean-up is complete.

11.7.5.1.16 The system is now ready to start running extracts. On the Foxy 200, push the blue softkey labeled "run".

11.7.5.1.17 Four options will appear, choose soft key A, which is entitled Run B. The drop former should come forward and position itself over the first vial and the program should start.

11.7.5.1.18 When the runs are complete, concentrate and combine the 2 resulting fractions into the same vial and then reduce the volume to 200-800uL. If further cleanups are required proceed to the appropriate section.

11.7.6 When all cleanups have been completed on the sample, add 20 ul of the labeled recovery standard spiking solution (see section 7.8.12) to an empty clean 1.1 ml tapered minivial. Mark the level of the recovery standard on the minivial (mark half the level, 10 µL, if the extracts are treated drinking waters). Label the minivial with the sample ID. Record the volume of recovery standard added on the benchsheet.

11.7.7 Transfer the concentrated extract into the mini-vial. Rinse the 40 ml vial twice with a small amount of hexane and add the rinses to the minivial. Put the minivial on the N-EVAP nitrogen blowdown and reduce the volume to the mark on the vial. Put the cap with PFTE-faced septa securely on the vial. Record the final extract volume on the benchsheet.

11.7.8 All items listed on the data review check list must be checked by both the prep analyst who performed the extraction and cleanups and the prep analyst who performed the second level review. An example data review check list is shown in Figure 4.

11.7.9 Transfer the extracts and paperwork to the GC/MS group for analysis.

11.8 Sample Extract Analysis

11.8.1 Analyze the sample extracts under the same instrument operating conditions used to perform the instrument calibrations. Inject 2 µL into the GC/MS and acquire data until OCDF has eluted from the column.

11.8.2 Record analysis information in the instrument logbook. The following information is required:

Date of analysis
Time of analysis
Instrument data system filename

Analyst
Lab sample identification

Additional information may be recorded in the logbook if necessary.

11.8.3 Generate ion chromatograms for the masses listed in Table 5 that encompass the expected retention windows of the PCDD and PCDF homologous series.

12. Data Analysis and Calculations

12.1 Qualitative identification criteria for PCDDs and PCDFs. For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

12.1.1 The ion current response for both ions used for quantitative purposes must reach maximum simultaneously (± 2 seconds).

12.1.2 The signal-to-noise ratio (S/N) for each GC peak at each exact m/z must be ≥ 2.5 for positive identification of a PCDD/PCDF compound.

12.1.3 The ratio of the integrated areas of the two exact m/z's specified in Table 5 must be within the limits specified in Table 6, or within ±10 percent of the ratio in the midpoint (CS3) calibration or the calibration verification (VER), whichever is most recent.

12.1.4 The relative retention time of the peak for a 2,3,7,8-substituted PCDD or PCDF must be within the limits in Table 8. The retention time of peaks representing non-2,3,7,8-substituted PCDDs/PCDFs must be within the retention time windows established in section 10.2.4.

12.2 Quantitation for PCDD's and PCDF's.

12.2.1 Calculate the Internal Standard and Cleanup Standard Recoveries (Ris) relative to the Recovery Standard according to the following equation:

$$Ris = \frac{Ais \times Qrs}{Ars \times RRFis \times Qis} \times 100\%$$

where:

Ais = sum of the areas of the quantitation ions of the appropriate internal standard (cleanup standard is single ion)
Ars = sum of the areas of the quantitation ions of the recovery standard
Qrs = ng of recovery standard added to extract
Qis = ng of internal standard added to sample
RRFis = mean relative response factor of internal standard obtained during initial calibration

Note: In some situations, such as high-volume water sampling, the extract is split for multiple analyses. In this case, Qrs must be correctly calculated to account for the splitting of extracts before the recovery standard was added.

$$Qrs = \frac{Crs \times Vrs}{S}$$

Where:

Qrs = ng of recovery standard added to extract
Crs = concentration of recovery standard added to the split portion of the extract
Vrs = volume of recovery standard added to the split portion of the extract
S = split ratio of the extract (decimal fraction of the extract used)

12.2.2 The split ratio represents the proportion of extract used from splits taken after the addition of internal standards and before the addition of recovery standards. The split ratio is calculated as the product of all split ratios generated between these steps:

$$S = Spis \times Spcs \times Spfc$$

Where:

Spis = the decimal fraction of extract used from split taken once the internal standard has been added and the extraction is performed.
Spcs = the decimal fraction of extract used from split taken once the cleanup standard (if used) has been added.
Spfc = the decimal fraction of extract used from split taken once the cleanup fractionation column has been run.

12.2.3 When properly applied, isotope dilution techniques produce results that are independent of recovery. The recovery of each internal standard should be within the limits specified in Table 13 or Table 14. If the recovery of any internal standard is not within the specified limits, calculate the S/N ratio of the internal standard. If the S/N is > 10 and the method minimum levels are met, report the data as is with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the minimum levels are not achieved, re-extract and re-analyze the sample. If the poor internal standard recovery is judged to be a result of sample matrix, a reduced portion of the sample may be re-extracted or additional clean-ups may be employed.

12.2.4 Calculate the concentration of target analytes according to the following equation:

$$C = \frac{Ata \times Qis}{Ais \times RRF \times Ws \times Ssl}$$

Where:

Ata = sum of the areas of the quantitation ions of the target analyte
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Qis = ng of internal standard added to sample

RRF = mean relative response factor from initial calibration.
Ws = amount of sample spiked and extracted (grams or liters)
Ssl = decimal expression of percent solids (optional, if results are requested to be reported on dry weight basis)

Note: The percent solids calculation is performed by the laboratory LIMS system prior to final reporting.

12.2.5 The concentrations of non-2,3,7,8-isomers are calculated using the RRF for the corresponding 2,3,7,8-isomer. If more than one 2,3,7,8-isomer exist for a particular level of chlorination, the average of the individual 2,3,7,8-isomer RRF's is used in the calculation.

12.2.6 Calculate the total concentration of all isomers within each homologous series of PCDD's and PCDF's by summing the concentrations of the individual PCDD or PCDF isomers.

12.2.7 If no peaks are present in the region of the ion chromatogram where the compounds of interest are expected to elute, calculate the estimated detection limit (EDL) for that compound according to the following equation:

$$EDL = \frac{N \times 2.5 \times Qis}{His \times RRFs \times Ws \times Ssl}$$

Where:
N = peak to peak noise of quantitation ion signal in the region of the ion chromatogram where the compound of interest is expected to elute
His = peak height of quantitation ion for appropriate internal standard
Qis = ng of internal standard added to sample
RRFs = mean relative response factor of compound for the shift opening and closing standards
W = amount of sample spiked and extracted (grams or liters)
Ssl = decimal expression of percent solids (optional, if results are requested to be reported on dry weight basis)

Note: The percent solids calculation is performed by the laboratory LIMS system prior to final reporting.

12.2.8 If peaks are present in the region of the ion chromatogram which do not meet the qualitative criteria listed in section 12.1.3, calculate an Estimated Maximum Possible Concentration (EMPC) using the equation in section 12.2.4, except that Ata should represent the sum of the area under the one peak and of the other peak area calculated using the theoretical chlorine isotope ratio. The peak selected to calculate the theoretical area should be the one which gives the lower of the two possible results (i.e. the EMPC will always be lower than the result calculated from the uncorrected areas).

12.2.9 If peaks are present in the diphenyl ether mass channel at the same retention time as a PCDF peak, the peak cannot be identified as a PCDF. Calculate the concentration of

the peak using the equation in section 12.2.4 but report the concentration as an Estimated Maximum Possible Concentration.

12.2.10 If the concentration in the final extract of any 2,3,7,8-substituted PCDD/PCDF isomer (except OCDD or OCDF) exceeds the upper method calibration limits, a dilution of the extract or a re-extraction of a smaller portion of the sample must be performed. For the other congeners (including OCDD and OCDF), however, report the measured concentration and indicate that the value exceeds the calibration limit by flagging the results with "E". Dilutions of up to 1/10 may be performed on the extract. If the compounds that exceed the calibration range cannot be brought within the calibration range by a 1/10 dilution, extraction of a smaller aliquot of sample may be performed or the sample may be analyzed by a more appropriate analytical technique such as HRGC/LRMS. Consultation with the client should occur before any re-extraction is performed.

12.2.11 Evaluate the ion chromatograms of the PFK lock mass and calibration mass for each MID group. The PFK mass intensity should be consistent through out the retention time of the target compounds. Negative excursions or variations in the PFK mass intensity indicate the elution of interferences from the GC column that are causing suppression in the ion source of the mass spectrometer. This ion suppression can reduce the instrument sensitivity and quantitative result of any peaks that elute at the same retention time. Either additional extract cleanup or dilutions can reduce ion suppression. The quantitative results should be carefully evaluated when there is evidence of ion suppression present in the PFK mass traces.

12.3 The DB-5 (RTX-5) column does not provide for isomer specificity of 2,3,7,8-TCDF using the operating condition required for this method. If a peak is determined to be present at the expected retention time of 2,3,7,8-TCDF and its calculated concentration is above the MinL, the sample extract must be analyzed on the DB-225 (RTX-225) column.

12.4 The Minimum Level (MinL) is defined as the level at which the instrument gives acceptable calibration assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures. Deviation from the extraction amounts or final volumes listed Table 2 changes the MinL. The MinL is calculated as shown in the following equation:

$$\text{MinL} = \frac{C\,\text{min} \times Vfe}{Ws}$$

Where:

Cmin = the concentration the analyte in the lowest calibration standard
Ws = amount of sample spiked and extracted (grams or liters)
Vfe = the final volume of the extract, corrected for all splits and dilutions

$$\text{Vfe} = \frac{Vdel \times DFpr}{Spr \times S}$$

Where:

Vdel = the volume of extract delivered to the analysis
DFpr = the dilution factor for dilutions performed to the final extract
Spr = the split ratio for any post-recovery standard splits
S = the split ratio for any post-internal standard and post-cleanup standard splits

12.5 The Maximum Level (MaxL) is defined as the concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. The MaxL is calculated as shown in the following equation:

$$MaxL = \frac{C\max \times Vfe}{Ws}$$

Where:

Cmax = the concentration the analyte in the highest calibration standard
Vfe and Ws are defined in Section 12.4.

12.6 Flag all compound results in the sample that were detected in the method blank with a "B" qualifier.

12.7 Flag all compound results in the sample that are below the minimum level with a "J" qualifier.

12.8 Flag all compound results in the sample that are above the upper calibration limit with an "E" qualifier.

12.9 Flag all compound results in the sample that are "Estimated Maximum Possible Concentrations" with a "Q" qualifier.

12.10 Flag compound results in the sample that may contain co-eluting compounds with a "C" qualifier.

12.11 Flag compound results in the sample that may be affected by ion suppression with a "S" qualifier.

12.12 Data review

12.12.1 The analyst who performs the initial data calculations must initial and date the front chromatogram of the raw data package to document that they have performed the qualitative and quantitative analysis on the sample data.

12.12.2 A second analyst must verify all qualitative peak identifications. If discrepancies are found, the data must be returned to the analyst who performed the initial peak identification for resolution.

12.12.3 A second analyst must check all hand calculation and data entry into calculation programs, databases, or spreadsheets at a frequency of 100 percent. If discrepancies are

found, the data must be returned to the analyst who performed the initial calculation for resolution.

12.12.4 The reviewing analyst must initial and date the front chromatogram of the raw data package to document that they have performed the second level review on the sample data.

12.12.5 All items listed on the data review check list must be checked by both the analyst who performed the initial qualitative and quantitative analysis and the analyst who performed the second level review. An example data review check list is shown in Figure 4.

13. Method Performance

13.1 The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience. Training records are filed with the QA department.

14. Pollution Prevention

14.1 All procedures shall be conducted in a manner to minimize, as far as practical, the use of solvents, reagents and other chemicals.

15. Waste Management

15.1 Waste generated in this procedure must be segregated and disposed according to the facility hazardous waste procedures.

16. References

16.1 Quality Assurance Management Plan. (current revision)

16.2 EPA Method 1613: Tetra- Through Octa- Chlorinated Dioxins And Furans by Isotope Dilutions HRGC/HRMS, Revision B, October 1994

16.3 STL SOP, KNOX-ID-0011, Preparation of Dioxin Standards, current revision.

16.11 STL SOP, KNOX-QA-0002, Glassware Cleaning, current revision.

17. Miscellaneous

17.1 Deviations from reference method.

17.1.1 Spiking levels have been reduced to minimize the amount of dioxin contaminated waste generated by this procedure. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.2 Method 1613B employs a gravimetric determination of sample size rather than a volumetric determination. This procedure employs a volumetric determination of sample size to allow reporting of sample concentration in the standard units of pg/L (ppq). This modification has no impact on the performance criteria of this method.

17.1.3 The amount of hexane used in the solvent exchange step has been reduced from that specified in the reference methods. The reduction in solvent used is a pollution prevention measure. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.4 Method 1613B specifies that the sample bottle is rinsed twice with 5 mL of reagent water after the sample is transferred to the separatory funnel. This procedure specifies that the sample bottle is rinsed three times with methylene chloride after the sample is transferred to the separatory funnel. This modification improves the removal of target compounds from the sample bottle.

17.1.5 The separatory funnel is only rinsed once with methylene chloride after the sample is extracted instead of three times as specified in Method 1613B. The reduction in solvent used is a pollution prevention measure. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.6 Toluene volumes and cycle rates for Soxhlet extractors have been optimized for the specific size of glassware used and may not be the same as those specified in the referenced method. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.7 Soxhlet extracts are not filtered before concentration and solvent exchange. The use of glass wool in the extraction thimbles eliminates the transfer of particles to the extraction solvent. The column cleanup procedures remove any particulate that may not be removed by the glass wool. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.8 Extraction amounts are based on wet weight as opposed to the adjusted amount based on percent moisture as specified in method 1613B. Particle size determination and reduction as specified in method 1613B is not performed on a routine basis. Silica and sand is not added to the Soxhlet extraction thimble as specified in method 1613B. Fish tissues are extracted with toluene rather than methylene chloride/hexane as specified in method 1613B. These procedures are considered to be outside the scope of the laboratories routine extraction procedures and are only performed on a client specific or project specific basis. These procedures, if required, will be specified and documented in the appropriate QAPP's.

17.1.9 Benzene is used to aid in dissolving the samples and/or extracts in hexane. It has been demonstrated that the performance criteria specified in the methods is not affected by this modification.

17.1.10 The absolute retention time requirements in Method 1613 section 15.4.1.1 is not required in this procedure. The routine maintenance required of GC columns when analyzing samples from hazardous waste sites makes this requirement virtually impossible to meet in a commercial laboratory environment. This requirement provides no additional quality assurance purpose beyond those already provided by the use of labeled internal standards and required relative retention time limits.

17.1.11 This procedure provides for additional calculation and reporting of sample specific detection limits and estimated maximum possible concentrations not required by Method 1613. These reporting conventions are similar to those required by EPA SW-846 Method 8290 and expected by data users familiar with EPA Office of Solid Waste program requirements.

17.1.12 The use of tetradecane as a final extract solvent is acceptable under this procedure. Tetradecane provides for better long-term stability of extracts and minimizes evaporative losses. GC conditions must be adjusted to optimize temperatures for the use of tetradecane.

17.1.13 Extracts are stored at room temperature rather than at <10 °C. The reference method requires that standards be stored at room temperature. Recovery studies performed by Cambridge Isotopes Laboratories (CIL) indicate freezing or refrigeration of standards causes problems with precipitation. CIL recommends the storage of standards and extracts at room temperature as long as they are protected from exposure to UV and evaporative losses.

17.1.14 The determination of solids content procedure used for aqueous samples is the same as the 1613B procedure used for solid samples rather than the 1613B procedure for aqueous samples. The aqueous sample procedure in 1613B is subject to error if the sample density is not exactly 1.0 g/mL.

17.2 Summary of modifications to SOP from previous revisions.

17.2.1 Removed sections 1.5 and 5.8 from revision 0.

17.2.2 Modified sections 1.1, 7.2.2, 8.4, 10.2.8, 10.3, 10.3.3, 10.3.4.1, 12.2.1 and Tables 3, 7, and 8 in revision 0.

17.2.3 Added sections, 12.2.9, 12.2.10, 12.9, 12.10, and 17.1.4 to revision 0.

17.2.4 Updated Figures 1 and 2.

17.2.5 All sample prep procedures were included in revision 2 rather than being in separate procedures. Significant modifications were made to sections 2, 5, 6, 7, and 11 to incorporate the additional prep information.

17.2.6 Modified sections 12.2.1, 12.2.3, 12.2.4 in revision 2.

17.2.7 Deleted sections 12.4.1, 12.4.2, 12.4.3 in revision 2.

17.2.8 Added sections 3.15, 3.31, 10.2.9 to revision 2

17.3 List of tables and figures referenced in the body of the SOP.

17.3.1 Table 1 - Polychlorinated Dibenzodioxins and Furans Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography (HRGC)/High Resolution Mass Spectrometry (HRMS).

17.3.2 Table 2 - Types of Matrices, Sample Sizes and 2,3,7,8-TCDD Based Method Calibration Limits (ppt).

17.3.3 Table 3 - Concentration of Calibration Solutions Containing Labeled and Unlabeled PCDDs and PCDFs.

17.3.4 Table 4 - Window Defining Mixture and Column Performance Mixture Composition.

17.3.5 Table 5 - Ions Specified For Selected Ion Monitoring For PCDDs and PCDFs.

17.3.6 Table 6 - Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs.

17.3.7 Table 7 - OPR Spiking Components, Concentrations.

17.3.8 Table 8 - Retention Time References, Quantitation References, and Relative Retention Times.

17.3.9 Table 9 - Acceptance Criteria for VER Standard When All CDDs/CDFs are Tested.

17.3.10 Table 10 - Acceptance Criteria for Performance Tests When All CDDs/CDFs are Tested.

17.3.11 Table 11 - Acceptance Criteria for VER Standard When Only Tetra Compounds are Tested.

17.3.12 Table 12 - Acceptance Criteria for Performance Tests When Only Tetra Compounds are Tested.

17.3.13 Table 13 - Labeled Compound Recovery in Samples When All PCDDs/PCDFs are Tested.

17.3.14 Table 14 - Labeled Compound Recovery in Samples When Only Tetra Compounds are Tested.

17.3.15 Figure 1 - Recommended GC Operating Conditions.

17.3.16 Figure 2 - Recommended MID Descriptors.

17.3.17 Figure 3 - Example Sample Prep Benchsheet

17.3.18 Figure 4 - Example Data Review Checklist.

17.3.19 Figure 5 - Method 1613B – Aqueous sample Extraction (Flowchart)

17.3.20 Figure 6 - Method 1613B - Solid Sample Extraction

17.3.21 Figure 7 - Method 1613B - Sample Cleanup

17.3.22 Figure 8- Analysis of PCDD's and PCDF's by HRGC/HRMS (Flowchart).

History of Revisions

HISTORY OF REVISION PAGE

REV NO.	DATE	PAGES AFFECTED	REASON FOR REVISION
0	02/26/97	All	Initial version of the SOP
1	08/31/99	All	Procedure review.
2	01/28/02	All	Procedure review.

Table 1

Polychlorinated Dibenzodioxins and Furans Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography (HRGC)/High Resolution Mass Spectrometry (HRMS)

PCDD's/PCDF's [1] Isomer/Congener	CAS Registry	Labeled Analog	CAS Registry
2,3,7,8-TCDD	1746-01-6	$^{13}C_{12}$-2,3,7,8-TCDD	76523-40-5
		$^{37}Cl_4$-2,3,7,8-TCDD	85508-50-5
Total TCDD	41903-57-5		
2,3,7,8-TCDF	51207-31-9	$^{13}C_{12}$-2,3,7,8-TCDF	89059-46-1
Total TCDF	55722-27-5		
1,2,3,7,8-PeCDD	40321-76-4	$^{13}C_{12}$-1,2,3,7,8-PeCDD	109719-79-1
Total PeCDD	36088-22-9		
1,2,3,7,8-PeCDF	57117-41-6	$^{13}C_{12}$-1,2,3,7,8-PeCDF	109719-77-9
2,3,4,7,8-PeCDF	57117-31-4	$^{13}C_{12}$-2,3,4,7,8-PeCDF	116843-02-8
Total PeCDF	30402-15-4		
1,2,3,4,7,8-HxCDD	39227-28-6	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	109719-80-4
1,2,3,6,7,8-HxCDD	57653-85-7	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	109719-81-5
1,2,3,7,8,9-HxCDD	19408-74-3	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	109719-82-6
Total HxCDD	34465-46-8		
1,2,3,4,7,8-HxCDF	70648-26-9	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	114423-98-2
1,2,3,6,7,8-HxCDF	57117-44-9	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	116843-03-9
2,3,4,6,7,8-HxCDF	60851-34-5	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	116843-05-1
1,2,3,7,8,9-HxCDF	72918-21-9	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	116843-04-0
Total HxCDF	55684-94-1		
1,2,3,4,6,7,8-HpCDD	35822-46-9	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	109719-83-7
Total HpCDD	37871-00-4		
1,2,3,4,6,7,8-HpCDF	67562-39-4	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	109719-84-8
1,2,3,4,7,8,9-HpCDF	55673-89-7	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	109719-94-0
Total HpCDF	38998-75-3		
OCDD	3268-87-9	$^{13}C_{12}$-OCDD	114423-97-1
OCDF	39001-02-0	none	

1. Polychlorinated dioxins and furans.

TCDD = Tetrachlorodibenzo-p-dioxin
PeCDD = Pentachlorodibenzo-p-dioxin
HxCDD = Hexachlorodibenzo-p-dioxin
HpCDD = Heptachlorodibenzo-p-dioxin
OCDD = Octachlorodibenzo-p-dioxin

TCDF = Tetrachlorodibenzofuran
PeCDF = Pentachlorodibenzofuran
HxCDF = Hexachlorodibenzofuran
HpCDF = Heptachlorodibenzofuran
OCDF = Octachlorodibenzofuran

Table 2

Types of Matrices, Sample Sizes and 2,3,7,8-TCDD Based Method Calibration Limits (ppt)

	Water	Soil	Tissue	Wipe	Air	Waste
Lower MCL [1]	0.01	1.0	1.0	10	10	10
Upper MCL [1]	4	400	400	4000	4000	4000
Weight (L or g)	1 L	10 g	10 g	Entire Sample	Entire Sample	1 g
IS Spiking Levels (ppt)	1	100	100	1000 pg	1000 pg	1000
Final Extr Vol. (µL)	20	20	20	20	20	20

1. For other congeners multiply the values by 1 for TCDF, by 5 for PeCDD/F, HxCDD/F, HpCDD/F and by 10 for OCDD/F

Table 3

Concentration of Calibration Solutions Containing Labeled and Unlabeled PCDDs and PCDFs

Analyte	CS1 (pg/µl)	CS2 (pg/µl)	CS3 (VER) (pg/µl)	CS4 (pg/µl)	CS5 (pg/µl)
2,3,7,8-TCDD	0.5	2.0	10	40	200
2,3,7,8-TCDF	0.5	2.0	10	40	200
1,2,3,7,8-PeCDD	2.5	10	50	200	1000
1,2,3,7,8-PeCDF	2.5	10	50	200	1000
2,3,4,7,8-PeCDF	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000
2,3,4,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000
OCDD	5.0	20	100	400	2000
OCDF	5.0	20	100	400	2000
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200
Labeled Cleanup Standard					
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2.0	10	40	200
Labeled Recovery Standard					
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

Table 4

Window Defining Mixture and Column Performance Mixture Composition

DB-5 (RTX-5) Column Window Defining Mixture

Congener	First Eluted	Last Eluted
TCDF	1,3,6,8-	1,2,8,9-
TCDD	1,3,6,8-	1,2,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
PeCDD	1,2,4,6,8-/ 1,2,4,7,9-	1,2,3,8,9-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HxCDD	1,2,4,6,7,9-/ 1,2,4,6,8,9-	1,2,3,4,6,7-
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

DB-5 (RTX-5) Column Performance Mixture

Isomer
1,2,3,7/1,2,3,8-TCDD
1,2,3,9-TCDD
2,3,7,8-TCDD

DB-225 (RTX-225) Column Performance Mixture

Isomer
2,3,4,7-TCDF
2,3,7,8-TCDF
1,2,3,9-TCDF

Table 5

Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs

Descriptor	Accurate Mass	Ion ID	Elemental Composition	Analyte
1	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9338	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (S)
	342.9792	QC	C_8F_{13}	PFK
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
2	330.9792	LOCK	C_7F_{13}	PFK
	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	380.9760	QC	C_8F_{15}	PFK
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	380.9760	LOCK	C_8F_{15}	PFK
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8156	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	404.9760	QC	$C_{10}F_{15}$	PFK
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE

Table 5 Continued

Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs

Descriptor	Accurate Mass	Ion ID	Elemental Composition	Analyte
4	404.9760	LOCK	$C_{10}F_{15}$	PFK
	407.7818	M+2	$C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0$	HpCDF
	409.7788	M+4	$C_{12}H\ ^{35}Cl_5\ ^{37}Cl_2\ 0$	HpCDF
	417.8250	M	$^{13}C_{12}H\ ^{35}Cl_7\ 0$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0$	HpCDF (S)
	423.7767	M+2	$C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0_2$	HpCDD
	425.7737	M+4	$C_{12}H\ ^{35}Cl_5\ ^{37}Cl_2\ 0_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H\ ^{35}Cl_6\ ^{37}Cl\ 0_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H\ ^{35}Cl_5\ ^{37}Cl_2\ 0_2$	HpCDD (S)
	442.9728	QC	$C_{10}F_{17}$	PFK
	479.7165	M+4	$C_{12}H\ ^{35}Cl_7\ ^{37}Cl_2\ 0$	NCDPE
5	430.9728	LOCK	C_9F_{17}	PFK
	441.7428	M+2	$C_{12}\ ^{35}Cl_7\ ^{37}Cl\ 0$	OCDF
	443.7399	M+4	$C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ 0$	OCDF
	457.7377	M+2	$C_{12}\ ^{35}Cl_7\ ^{37}Cl\ 0_2$	OCDD
	459.7348	M+4	$C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ 0_2$	OCDD
	469.7780	M+2	$^{13}C_{12}\ ^{35}Cl_7\ ^{37}Cl\ 0_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ 0_2$	OCDD (S)
	480.9696	QC	$C_{10}F_{19}$	PFK
	513.6775	M+4	$C_{12}\ ^{35}Cl_8\ ^{37}Cl_2\ 0$	DCDPE

1. Nuclidic masses used:

H = 1.007825 C = 12.00000 ^{13}C = 13.003355 F = 18.9984
O = 15.994915 ^{35}Cl = 34.968853 ^{37}Cl = 36.965903

Table 6

Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits	
			Lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6[(a)]	M/M+2	0.51	0.43	0.59
7[(b)]	M/M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

(a) Used for ^{13}C-HxCDF (IS).
(b) Used for ^{13}C-HpCDF (IS).

Table 7

OPR Spiking Components and Concentrations

Analyte	Spiking Solution Conc. (ng/ml)[1]	Spike Conc. Water (pg/L)[2]	Spike Conc. Solid (pg/g)[2]
2,3,7,8-TCDD	0.2	200	20
2,3,7,8-TCDF	0.2	200	20
1,2,3,7,8-PeCDD	1.0	1000	100
1,2,3,7,8-PeCDF	1.0	1000	100
2,3,4,7,8-PeCDF	1.0	1000	100
1,2,3,4,7,8-HxCDD	1.0	1000	100
1,2,3,6,7,8-HxCDD	1.0	1000	100
1,2,3,7,8,9-HxCDD	1.0	1000	100
1,2,3,4,7,8-HxCDF	1.0	1000	100
1,2,3,6,7,8-HxCDF	1.0	1000	100
2,3,4,6,7,8-HxCDF	1.0	1000	100
1,2,3,7,8,9-HxCDF	1.0	1000	100
1,2,3,4,6,7,8-HpCDD	1.0	1000	100
1,2,3,4,6,7,8-HpCDF	1.0	1000	100
1,2,3,4,7,8,9-HpCDF	1.0	1000	100
OCDD	2.0	2000	200
OCDF	2.0	2000	200

1 - 1.0 mL of this solution is added to the OPR sample before extraction (see section 7.8.2).

2 - Spike concentrations are based on 1.0 L or 10.0g extraction.

Table 8

Retention Time References, Quantitation References, and Relative Retention Times

CDD/CDF	Retention time and quantitation reference	Relative retention time
Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the recovery standard		
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF	0.999-1.003
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	0.999-1.002
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF	0.999-1.002
2,3,4,7,8-PeCDF	$^{13}C_{12}$-2,3,4,7,8-PeCDF	0.999-1.002
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	0.999-1.002
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD	0.923-1.103
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.976-1.043
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.989-1.052
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.425
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.011-1.526
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.567
Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the recovery standard		
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	0.999-1.001
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	0.997-1.005
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	0.999-1.001
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	0.999-1.001
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	0.999-1.001
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	0.998-1.004
1,2,3,7,8,9-HxCDD	--[1]	1.000-1.019
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	0.999-1.001
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	0.999-1.001
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	0.999-1.001
OCDF	$^{13}C_{12}$-OCDD	0.999-1.008
OCDD	$^{13}C_{12}$-OCDD	0.999-1.001
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.944-0.970
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.949-0.975
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977-1.047
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.959-1.021
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977-1.000
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.981-1.003
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.043-1.085
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.057-1.151
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.086-1.110
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.032-1.311

1. The retention time reference for 1,2,3,7,8,9-HxCDD is $^{13}C_{12}$-1,2,3,6,7,8-HxCDD. 1,2,3,7,8,9-HxCDD is quantified using the averaged responses for $^{13}C_{12}$-1,2,3,4,7,8-HxCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD.

Table 9

Acceptance Criteria for VER Standard When All CDDs/CDFs are Tested[1]

CDD/CDF	Test conc (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	7.8-12.9
2,3,7,8-TCDF	10	8.4-12.0
1,2,3,7,8-PeCDD	50	39-65
1,2,3,7,8-PeCDF	50	41-60
2,3,4,7,8-PeCDF	50	41-61
1,2,3,4,7,8-HxCDD	50	39-64
1,2,3,6,7,8-HxCDD	50	39-64
1,2,3,7,8,9-HxCDD	50	41-61
1,2,3,4,7,8-HxCDF	50	45-56
1,2,3,6,7,8-HxCDF	50	44-57
2,3,4,6,7,8-HxCDF	50	44-57
1,2,3,7,8,9-HxCDF	50	45-56
1,2,3,4,6,7,8-HpCDD	50	43-58
1,2,3,4,6,7,8-HpCDF	50	45-55
1,2,3,4,7,8,9-HpCDF	50	43-58
OCDD	100	79-126
OCDF	100	63-159
$^{13}C_{12}$-2,3,7,8-TCDD	100	82-121
$^{13}C_{12}$-2,3,7,8-TCDF	100	71-140
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	62-160
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	76-130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	77-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	85-117
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	85-118
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	76-131
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	70-143
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	73-137
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	74-135
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	72-138
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	78-129
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	77-129
$^{13}C_{12}$-OCDD	200	96-415
$^{37}Cl_4$-2,3,7,8-TCDD	10	7.9-12.7

1. All specifications are given as concentration in the VER standard.

Table 10

Acceptance Criteria for Performance Tests When All CDDs/CDFs are Tested[1]

CDD/CDF	Test conc (ng/mL)	IPR[2,3] s (ng/mL)	IPR[2,3] X (ng/ml)	OPR (ng/mL)
2,3,7,8-TCDD	10	2.8	8.3-12.9	6.7-15.8
2,3,7,8-TCDF	10	2.0	8.7-13.7	7.5-15.8
1,2,3,7,8-PeCDD	50	7.5	38-66	35-71
1,2,3,7,8-PeCDF	50	7.5	43-62	40-67
2,3,4,7,8-PeCDF	50	8.6	36-75	34-80
1,2,3,4,7,8-HxCDD	50	9.4	39-76	35-82
1,2,3,6,7,8-HxCDD	50	7.7	42-62	38-67
1,2,3,7,8,9-HxCDD	50	11.1	37-71	32-81
1,2,3,4,7,8-HxCDF	50	8.7	41-59	36-67
1,2,3,6,7,8-HxCDF	50	6.7	46-60	42-65
2,3,4,6,7,8-HxCDF	50	7.4	37-74	35-78
1,2,3,7,8,9-HxCDF	50	6.4	42-61	39-65
1,2,3,4,6,7,8-HpCDD	50	7.7	38-65	35-70
1,2,3,4,6,7,8-HpCDF	50	6.3	45-56	41-61
1,2,3,4,7,8,9-HpCDF	50	8.1	43-63	39-69
OCDD	100	19	89-127	78-144
OCDF	100	27	74-146	63-170
$^{13}C_{12}$-2,3,7,8-TCDD	50	18.5	14-67	10-87.5
$^{13}C_{12}$-2,3,7,8-TCDF	50	17.5	15.5-56.5	11-76.0
$^{13}C_{12}$-1,2,3,7,8-PeCDD	50	19.5	13.5-92	10.5-113.5
$^{13}C_{12}$-1,2,3,7,8-PeCDF	50	17.0	13.5-78	10.5-96
$^{13}C_{12}$-2,3,4,7,8-PeCDF	50	19.0	8-139.5	6.5-164
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	50	20.5	14.5-73.5	10.5-96.5
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	50	19.0	17-61	12.5-81.5
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	50	21.5	13.5-76	9.5-101
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	50	17.5	15-61	10.5-79.5
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	50	18.5	14.5-68	11-88
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	50	20.0	12-78.5	8.5-102.5
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	50	17.5	17-64.5	13-83
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	50	20.5	16-55	10.5-79
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	50	20.0	14-70.5	10-93
$^{13}C_{12}$-OCDD	100	47.5	20.5-138	13-198.5
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.6	3.9-15.4	3.1-19.1

1. All specifications are given as concentration in the final extract, assuming a 20-µL volume.
2. s = standard deviation of the concentration
3. X = average concentration

Table 11

Acceptance Criteria for VER Standard When Only Tetra Compounds are Tested[1]

CDD/CDF	Test conc (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	8.2-12.3
2,3,7,8-TCDF	10	8.6-11.6
$^{13}C_{12}$-2,3,7,8-TCDD	100	85-117
$^{13}C_{12}$-2,3,7,8-TCDF	100	76-131
$^{37}Cl_4$-2,3,7,8-TCDD	10	8.3-12.1

1. All specifications are given as concentration in the VER standard.

Table 12

Acceptance Criteria for Performance Tests When Only Tetra Compounds are Tested[1]

CDD/CDF	Test conc (ng/mL)	IPR[2,3]		OPR (ng/mL)
		s (ng/mL)	X (ng/ml)	
2,3,7,8-TCDD	10	2.7	8.7-12.4	7.3-14.6
2,3,7,8-TCDF	10	2.0	9.1-13.1	8.0-14.7
$^{13}C_{12}$-2,3,7,8-TCDD	50	17.5	16-57.5	12.5-70.5
$^{13}C_{12}$-2,3,7,8-TCDF	50	17	17.5-49.5	13-63
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.4	4.5-13.4	3.7-15.8

1. All specifications are given as concentration in the final extract, assuming a 20-µL volume.
2. s = standard deviation of the concentration
3. X = average concentration

Table 13

Labeled Compound Recovery in Samples When All PCDDs/PCDFs are Tested

Compound	Spiking Solution Conc. (ng/mL)[1]	Test Conc. (ng/mL)[3]	Labeled Compound Recovery (ng/mL)[3]	(%)
Internal Standards				
$^{13}C_{12}$-2,3,7,8-TCDD	1.0	50	12.5-82.0	25-164
$^{13}C_{12}$-2,3,7,8-TCDF	1.0	50	12.0-84.5	24-169
$^{13}C_{12}$-1,2,3,7,8-PeCDD	1.0	50	12.5-90.5	25-181
$^{13}C_{12}$-1,2,3,7,8-PeCDF	1.0	50	12.0-92.5	24-185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	1.0	50	10.5-89.0	21-178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	1.0	50	16.0-70.5	32-141
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1.0	50	14.0-65.0	28-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1.0	50	13.0-76.0	26-152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	1.0	50	13.0-61.5	26-123
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	1.0	50	14.0-68.0	28-136
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	1.0	50	14.5-73.5	29-147
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1.0	50	11.5-70.0	23-140
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1.0	50	14.0-71.5	28-143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	1.0	50	13.0-69.0	26-138
$^{13}C_{12}$-OCDD	2.0	100	17.0-157	17-157
Cleanup Standard[2]				
$^{37}Cl_4$-2,3,7,8-TCDD [2]	0.2	10	3.5-19.7	35-197

1. 1.0 mL of the Internal Standard Spiking Solution is added to each sample, method blank and OPR sample prior to extraction (see section 7.8.4).

2. 1.0 mL of the Cleanup Standard Spiking Solution is added to each sample, method blank and OPR sample prior to extract cleanup (see section 7.8.8).

3. Specifications given as concentration in the final extract, assuming a 20-µL volume

Table 14

Labeled Compound Recovery in Samples When Only Tetra Compounds are Tested

Compound	Test conc, (ng/mL)	Labeled compound recovery (ng/mL)[1]	(%)
$^{13}C_{12}$-2,3,7,8-TCDD	50	15.5-68.5	31-137
$^{13}C_{12}$-2,3,7,8-TCDF	50	14.5-70.0	29-140
$^{37}Cl_4$-2,3,7,8-TCDD	10	4.2-16.4	42-164

1. Specifications given as concentration in the final extract, assuming a 20-µL volume

Figure 1

Recommended GC Operating Conditions

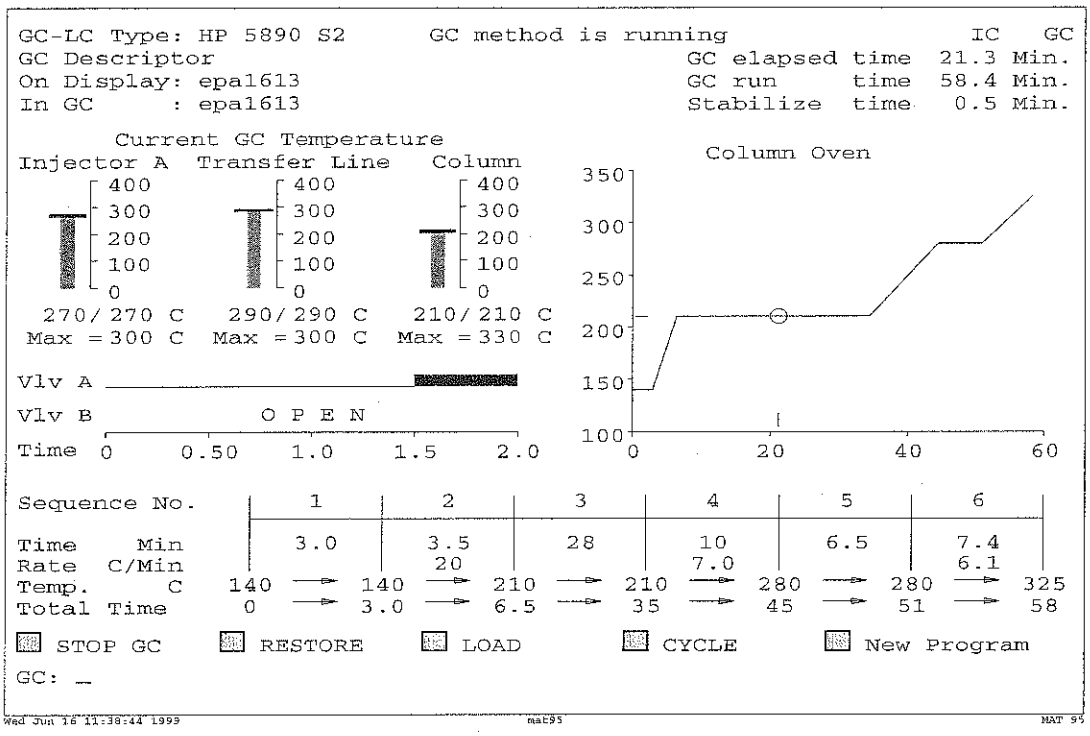
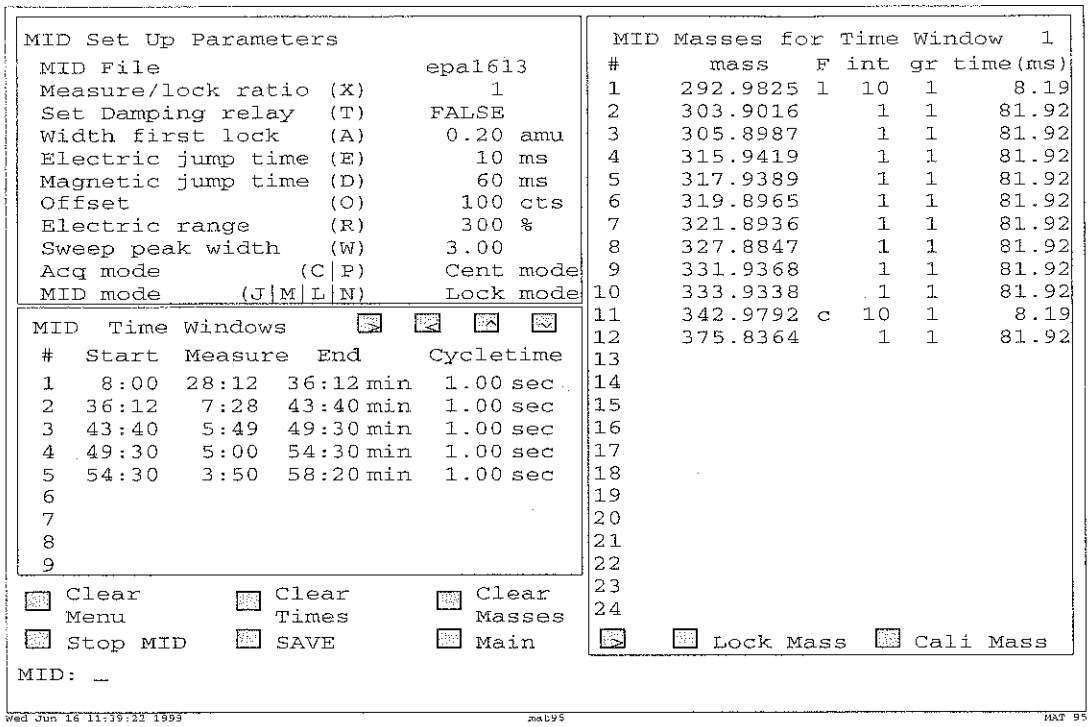


Figure 2

Recommended MID Descriptors



MID Set Up Parameters

MID File		epa1613
Measure/lock ratio	(X)	1
Set Damping relay	(T)	FALSE
Width first lock	(A)	0.20 amu
Electric jump time	(E)	10 ms
Magnetic jump time	(D)	60 ms
Offset	(O)	100 cts
Electric range	(R)	300 %
Sweep peak width	(W)	3.00
Acq mode	(C|P)	Cent mode
MID mode	(J|M|L|N)	Lock mode

MID Time Windows

#	Start	Measure	End	Cycletime
1	8:00	28:12	36:12 min	1.00 sec
2	36:12	7:28	43:40 min	1.00 sec
3	43:40	5:49	49:30 min	1.00 sec
4	49:30	5:00	54:30 min	1.00 sec
5	54:30	3:50	58:20 min	1.00 sec
6				
7				
8				
9				

Clear Menu | Clear Times | Clear Masses
Stop MID | SAVE | Main

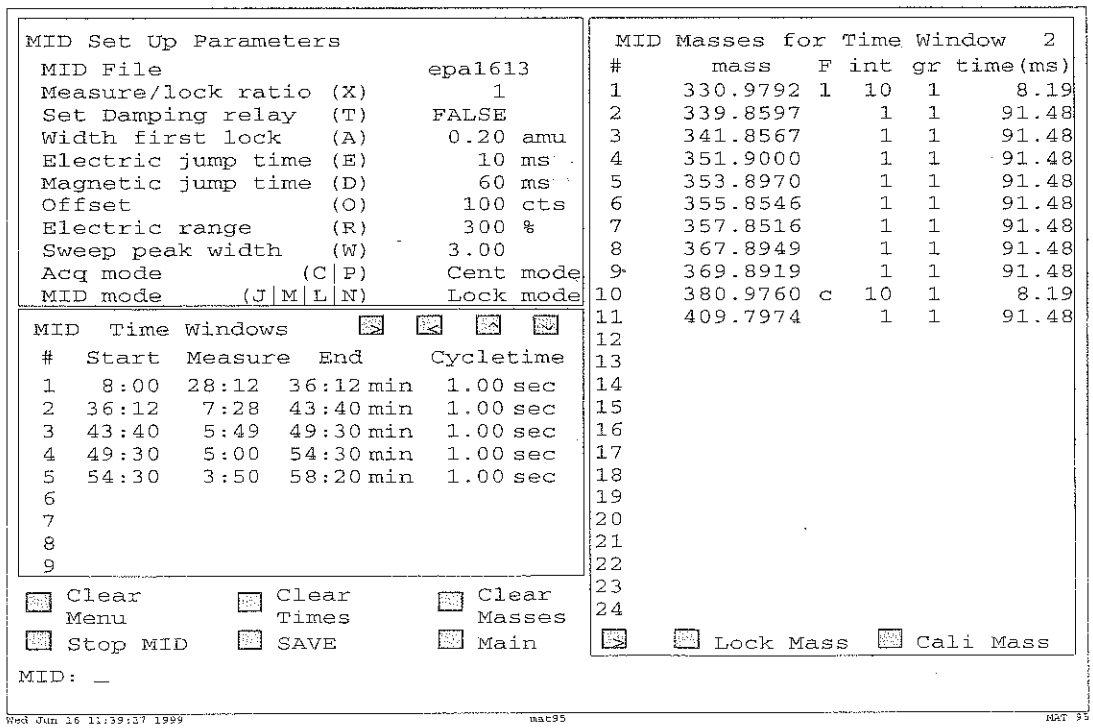
MID: _

MID Masses for Time Window 1

#	mass	F	int	gr	time(ms)
1	292.9825	l	10	1	8.19
2	303.9016		1	1	81.92
3	305.8987		1	1	81.92
4	315.9419		1	1	81.92
5	317.9389		1	1	81.92
6	319.8965		1	1	81.92
7	321.8936		1	1	81.92
8	327.8847		1	1	81.92
9	331.9368		1	1	81.92
10	333.9338		1	1	81.92
11	342.9792	c	10	1	8.19
12	375.8364		1	1	81.92
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					

Lock Mass | Cali Mass

Wed Jun 16 11:39:22 1999 mat95 MAT 95



MID Set Up Parameters

MID File		epa1613
Measure/lock ratio	(X)	1
Set Damping relay	(T)	FALSE
Width first lock	(A)	0.20 amu
Electric jump time	(E)	10 ms
Magnetic jump time	(D)	60 ms
Offset	(O)	100 cts
Electric range	(R)	300 %
Sweep peak width	(W)	3.00
Acq mode	(C|P)	Cent mode
MID mode	(J|M|L|N)	Lock mode

MID Time Windows

#	Start	Measure	End	Cycletime
1	8:00	28:12	36:12 min	1.00 sec
2	36:12	7:28	43:40 min	1.00 sec
3	43:40	5:49	49:30 min	1.00 sec
4	49:30	5:00	54:30 min	1.00 sec
5	54:30	3:50	58:20 min	1.00 sec
6				
7				
8				
9				

Clear Menu | Clear Times | Clear Masses
Stop MID | SAVE | Main

MID: _

MID Masses for Time Window 2

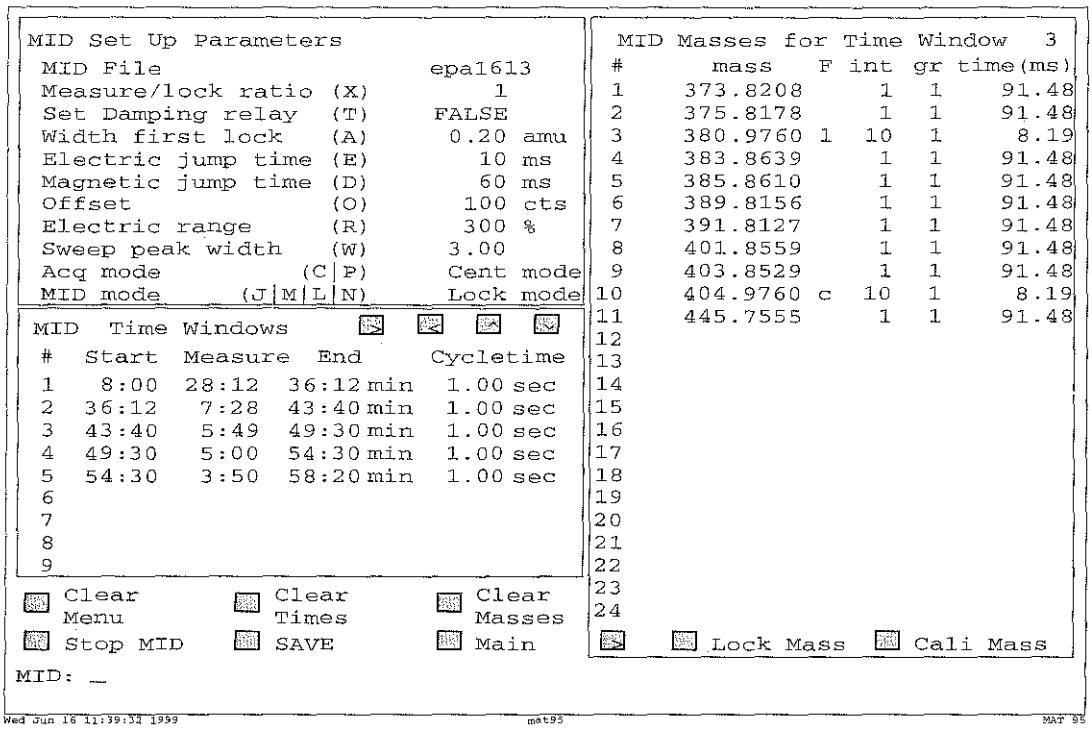
#	mass	F	int	gr	time(ms)
1	330.9792	l	10	1	8.19
2	339.8597		1	1	91.48
3	341.8567		1	1	91.48
4	351.9000		1	1	91.48
5	353.8970		1	1	91.48
6	355.8546		1	1	91.48
7	357.8516		1	1	91.48
8	367.8949		1	1	91.48
9	369.8919		1	1	91.48
10	380.9760	c	10	1	8.19
11	409.7974		1	1	91.48
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					

Lock Mass | Cali Mass

Wed Jun 16 11:39:17 1999 mat95 MAT 95

Figure 2 **Continued**

Recommended MID Descriptors



MID Set Up Parameters

MID File		epa1613
Measure/lock ratio	(X)	1
Set Damping relay	(T)	FALSE
Width first lock	(A)	0.20 amu
Electric jump time	(E)	10 ms
Magnetic jump time	(D)	60 ms
Offset	(O)	100 cts
Electric range	(R)	300 %
Sweep peak width	(W)	3.00
Acq mode	(C|P)	Cent mode
MID mode	(J|M|L|N)	Lock mode

MID Time Windows

#	Start	Measure	End	Cycletime
1	8:00	28:12	36:12 min	1.00 sec
2	36:12	7:28	43:40 min	1.00 sec
3	43:40	5:49	49:30 min	1.00 sec
4	49:30	5:00	54:30 min	1.00 sec
5	54:30	3:50	58:20 min	1.00 sec
6				
7				
8				
9				

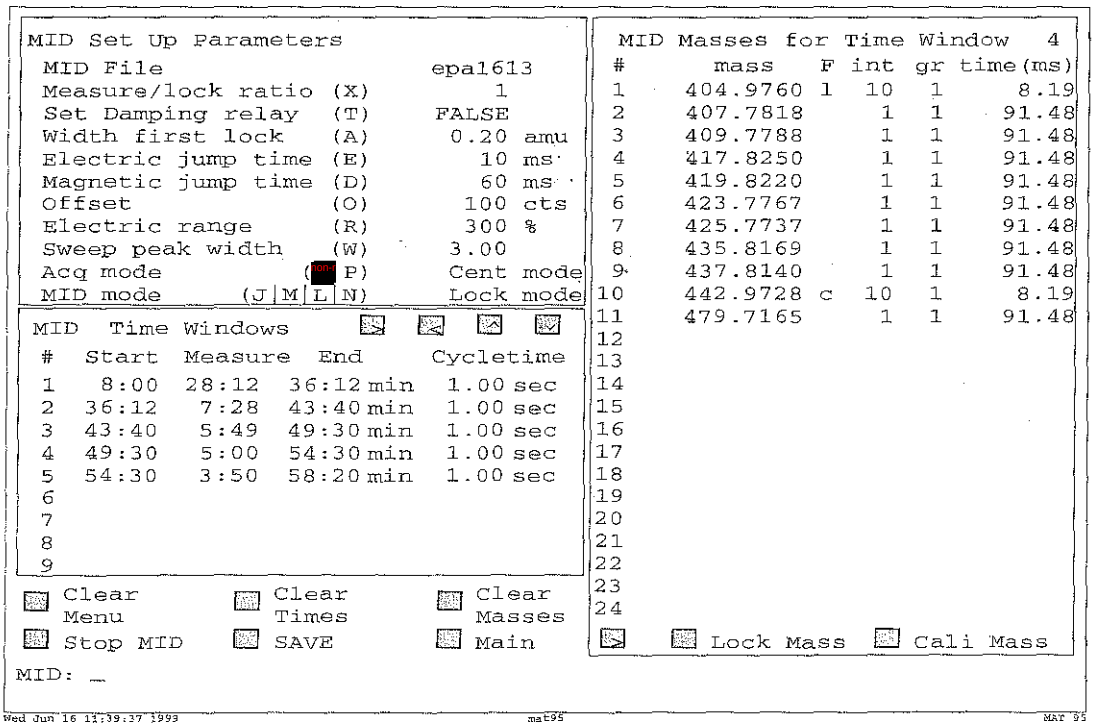
MID Masses for Time Window 3

#	mass	F	int	gr	time(ms)
1	373.8208		1	1	91.48
2	375.8178		1	1	91.48
3	380.9760	l	10	1	8.19
4	383.8639		1	1	91.48
5	385.8610		1	1	91.48
6	389.8156		1	1	91.48
7	391.8127		1	1	91.48
8	401.8559		1	1	91.48
9	403.8529		1	1	91.48
10	404.9760	c	10	1	8.19
11	445.7555		1	1	91.48
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					

Clear Menu | Clear Times | Clear Masses
Stop MID | SAVE | Main
Lock Mass | Cali Mass

MID: _

Wed Jun 16 11:39:32 1999 mat95 MAT 95



MID Set Up Parameters

MID File		epa1613
Measure/lock ratio	(X)	1
Set Damping relay	(T)	FALSE
Width first lock	(A)	0.20 amu
Electric jump time	(E)	10 ms
Magnetic jump time	(D)	60 ms
Offset	(O)	100 cts
Electric range	(R)	300 %
Sweep peak width	(W)	3.00
Acq mode	(C|P)	Cent mode
MID mode	(J|M|L|N)	Lock mode

MID Time Windows

#	Start	Measure	End	Cycletime
1	8:00	28:12	36:12 min	1.00 sec
2	36:12	7:28	43:40 min	1.00 sec
3	43:40	5:49	49:30 min	1.00 sec
4	49:30	5:00	54:30 min	1.00 sec
5	54:30	3:50	58:20 min	1.00 sec
6				
7				
8				
9				

MID Masses for Time Window 4

#	mass	F	int	gr	time(ms)
1	404.9760	l	10	1	8.19
2	407.7818		1	1	91.48
3	409.7788		1	1	91.48
4	417.8250		1	1	91.48
5	419.8220		1	1	91.48
6	423.7767		1	1	91.48
7	425.7737		1	1	91.48
8	435.8169		1	1	91.48
9	437.8140		1	1	91.48
10	442.9728	c	10	1	8.19
11	479.7165		1	1	91.48
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					

Clear Menu | Clear Times | Clear Masses
Stop MID | SAVE | Main
Lock Mass | Cali Mass

MID: _

Wed Jun 16 11:39:37 1999 mat95 MAT 95

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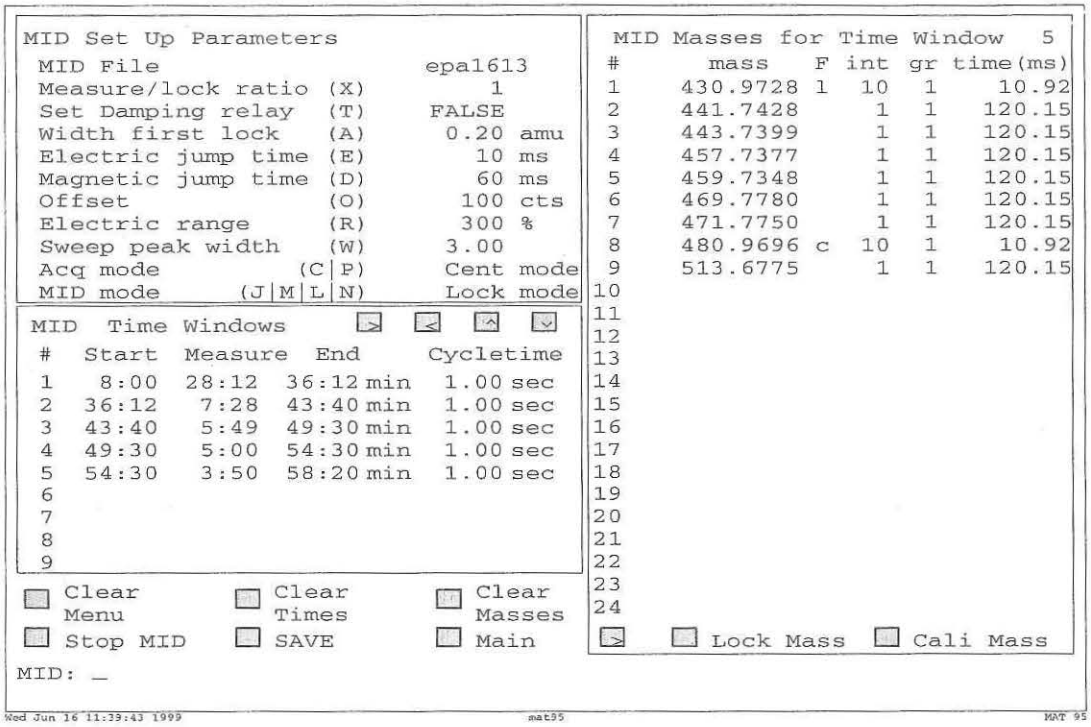
Figure 2 Continued

Recommended MID Descriptors



MID Set Up Parameters

MID File		epa1613
Measure/lock ratio	(X)	1
Set Damping relay	(T)	FALSE
Width first lock	(A)	0.20 amu
Electric jump time	(E)	10 ms
Magnetic jump time	(D)	60 ms
Offset	(O)	100 cts
Electric range	(R)	300 %
Sweep peak width	(W)	3.00
Acq mode	(C|P)	Cent mode
MID mode	(J|M|L|N)	Lock mode

MID Time Windows

#	Start	Measure	End	Cycletime
1	8:00	28:12	36:12 min	1.00 sec
2	36:12	7:28	43:40 min	1.00 sec
3	43:40	5:49	49:30 min	1.00 sec
4	49:30	5:00	54:30 min	1.00 sec
5	54:30	3:50	58:20 min	1.00 sec
6				
7				
8				
9				

Clear Menu | Clear Times | Clear Masses
Stop MID | SAVE | Main

MID: _

MID Masses for Time Window 5

#	mass	F	int	gr	time(ms)
1	430.9728	l	10	1	10.92
2	441.7428		1	1	120.15
3	443.7399		1	1	120.15
4	457.7377		1	1	120.15
5	459.7348		1	1	120.15
6	469.7780		1	1	120.15
7	471.7750		1	1	120.15
8	480.9696	c	10	1	10.92
9	513.6775		1	1	120.15
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					
23					
24					

Lock Mass | Cali Mass

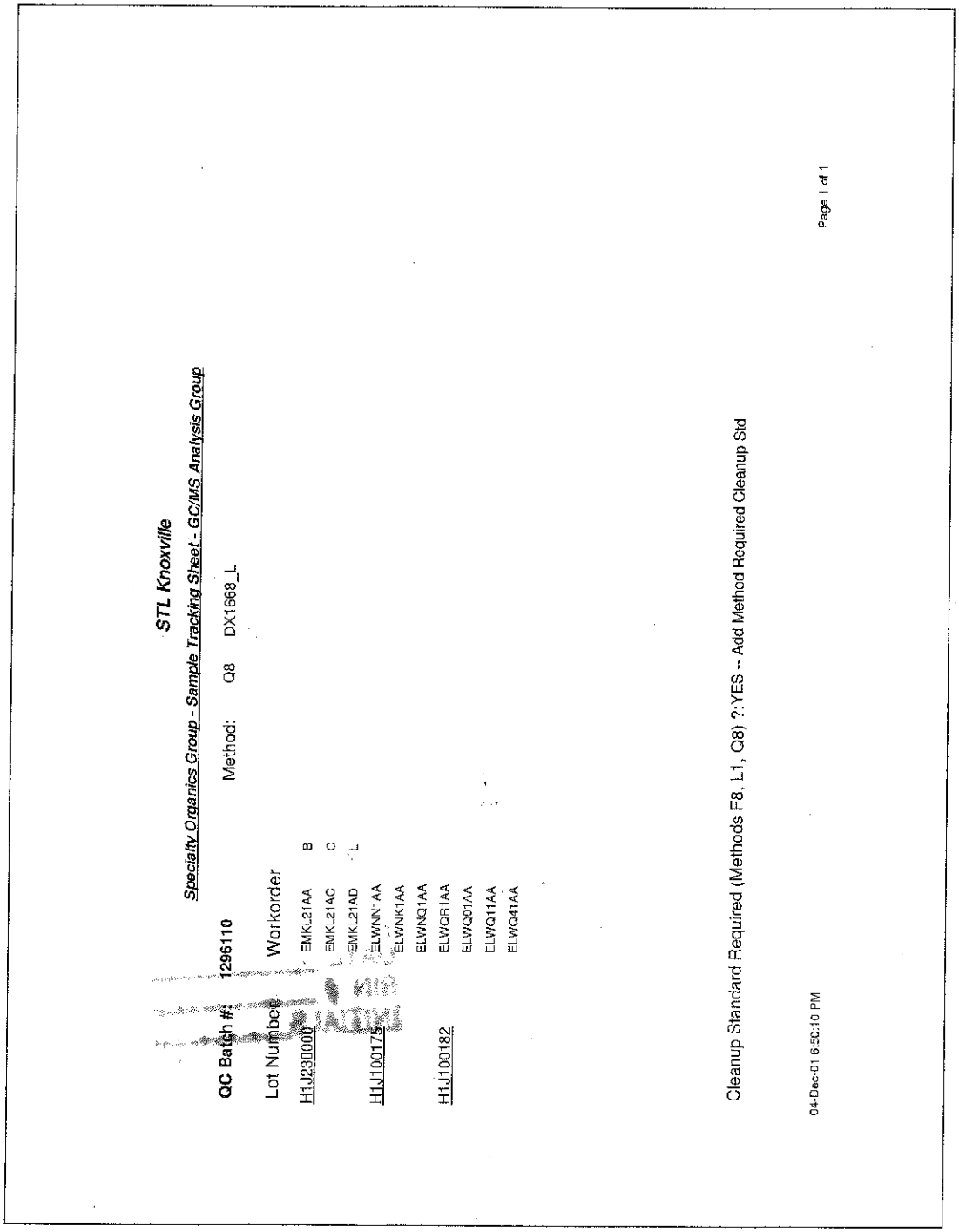
Wed Jun 16 11:39:43 1999 mat95 MAT 95

DATE 8/7/2018
RIN # 20180041691
INITIALS

AK5 042081

Figure 3

Example Sample Prep Benchsheets



STL Knoxville

Specialty Organics Group - Sample Tracking Sheet - GC/MS Analysis Group

QC Batch #: 1296110 Method: Q8 DX1668_L

Lot Number	Workorder		
H1J230000	EMKL21AA	B	
	EMKL21AC	C	
	EMKL21AD	L	
H1J100175	ELWNN1AA		
	ELWNK1AA		
	ELWNQ1AA		
H1J100182	ELWQR1AA		
	ELWQQ1AA		
	ELWQ11AA		
	ELWQ41AA		

Cleanup Standard Required (Methods F8, L1, Q8) ?:YES -- Add Method Required Cleanup Std

04-Dec-01 6:50:10 PM

Page 1 of 1

Figure 3 Continued

Example Sample Prep Benchsheets

STL Knoxville

Specialty Organics Group - Sample Tracking Sheet - GC/MS Analysis Group

QC Batch No 1296110 Relinquished to GC/MS By: _____ Date: _____

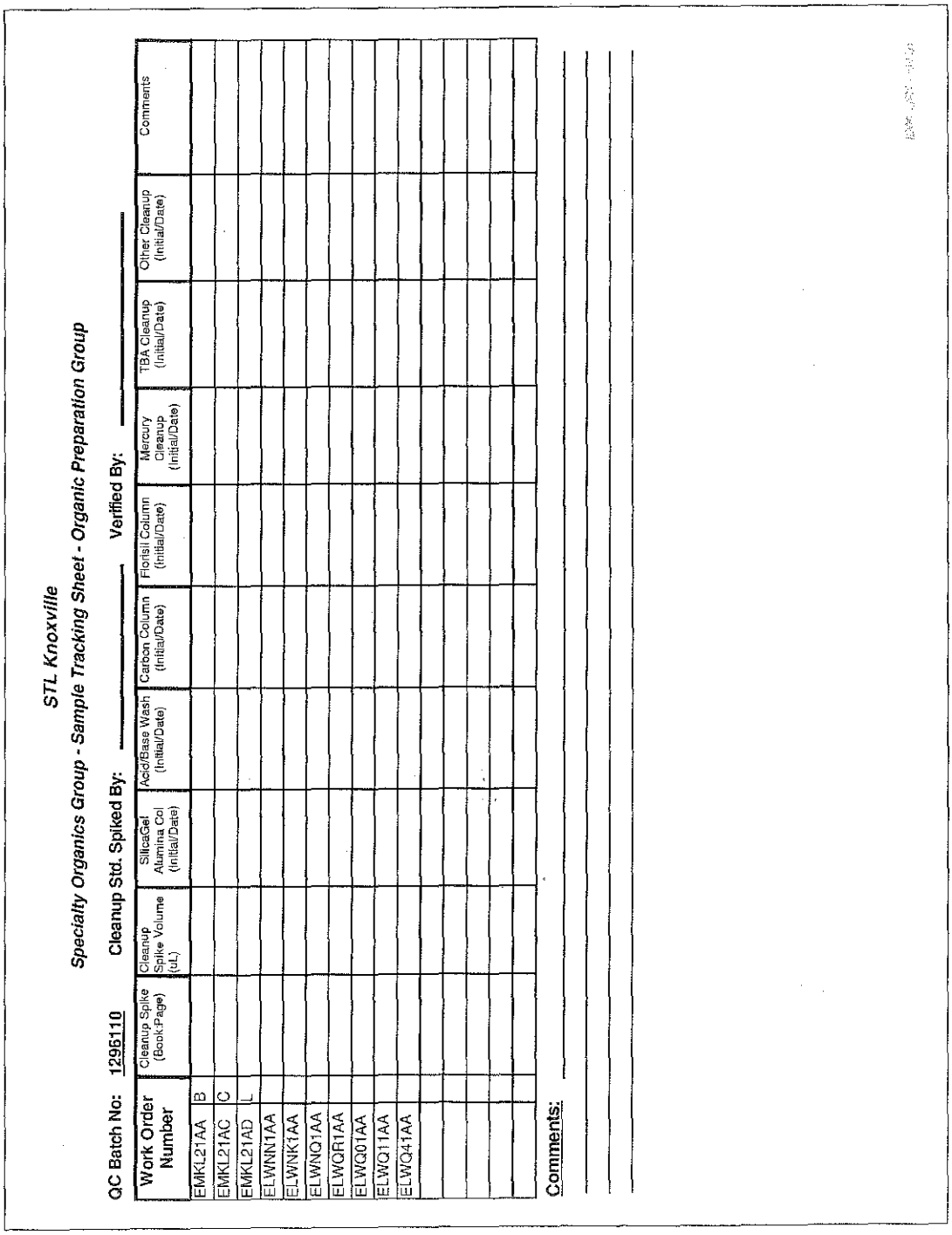
Received in GC/MS By: _____ Date: _____

Work Order Numbe		Column: DB-5 or RTX-:				Column: SPB-Oct				Column: DB-225 or RTX-22:			
		Date	Instrument	Analyst	Code	Date	Instrument	Analyst	Code	Date	Instrument	Analyst	Code
EMKL21AA	B												
EMKL21AC	C												
EMKL21AD	L												
ELWNN1AA													
ELWNK1AA													
ELWNQ1AA													
ELWQR1AA													
ELWQ01AA													
ELWQ11AA													
ELWQ41AA													

Comments: _____

Figure 3 Continued

Example Sample Prep Benchsheets



STL Knoxville

Specialty Organics Group - Sample Tracking Sheet - Organic Preparation Group

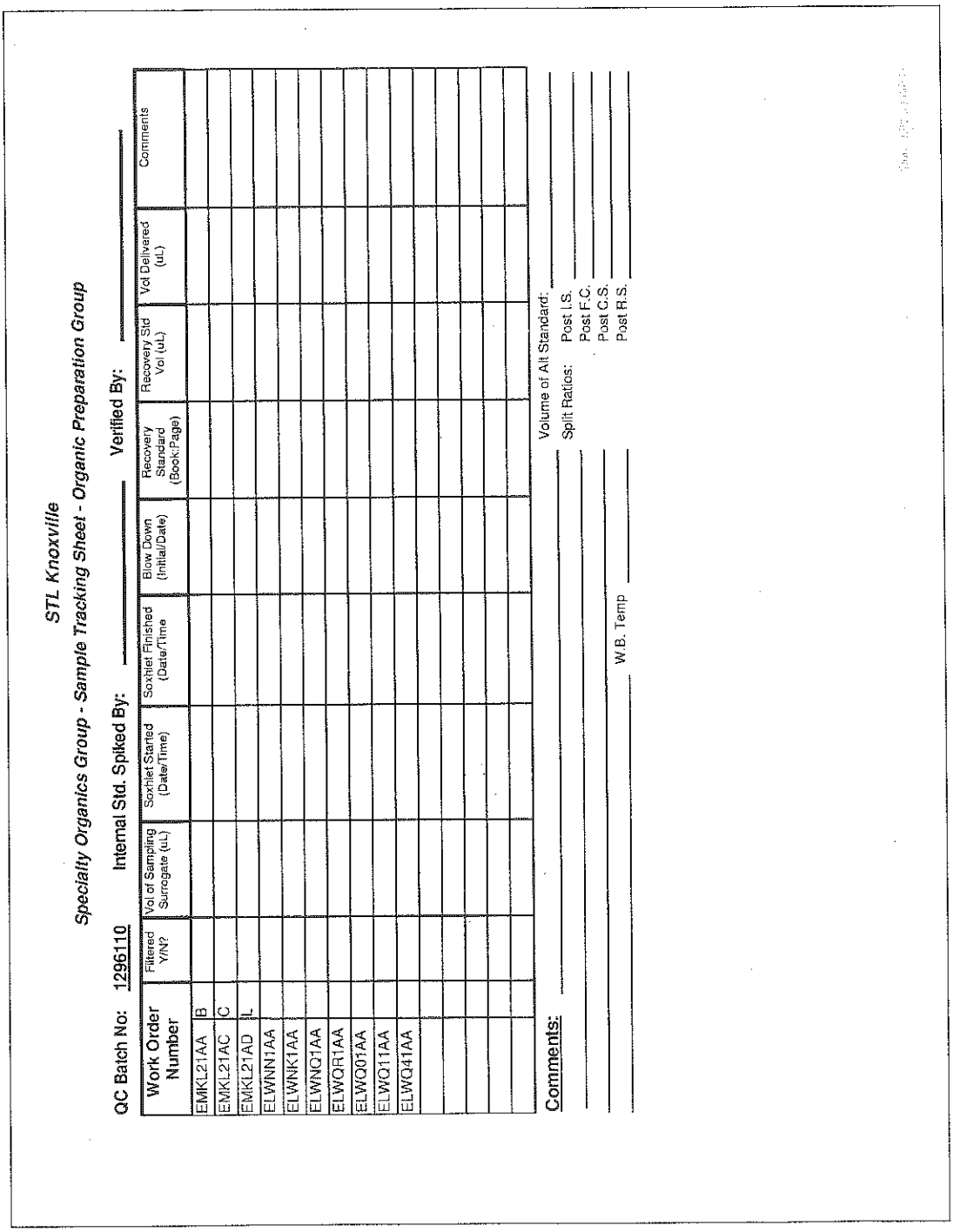
QC Batch No: 1296110 Cleanup Std. Spiked By: _____ Verified By: _____

Work Order Number		Cleanup Spike (Book-Page)	Cleanup Spike Volume (uL)	SilicaGel Alumina Col (Initial/Date)	Acid/Base Wash (Initial/Date)	Carbon Column (Initial/Date)	Florisil Column (Initial/Date)	Mercury Cleanup (Initial/Date)	TBA Cleanup (Initial/Date)	Other Cleanup (Initial/Date)	Comments
EMKL21AA	B										
EMKL21AC	C										
EMKL21AD	L										
ELWNN1AA											
ELWNK1AA											
ELWNQ1AA											
ELWQR1AA											
ELWQ01AA											
ELWQ11AA											
ELWQ41AA											

Comments: _____

Figure 3 Continued

Example Sample Prep Benchsheets



STL Knoxville

Specialty Organics Group - Sample Tracking Sheet - Organic Preparation Group

QC Batch No: 1296110 Internal Std. Spiked By: _____ Verified By: _____

Work Order Number		Filtered Y/N?	Vol of Sampling Surrogate (uL)	Soxhlet Started (Date/Time)	Soxhlet Finished (Date/Time	Blow Down (Initial/Date)	Recovery Standard (Book:Page)	Recovery Std Vol (uL)	Vol Delivered (uL)	Comments
EMKL21AA	B									
EMKL21AC	C									
EMKL21AD	L									
ELWNN1AA										
ELWNK1AA										
ELWNQ1AA										
ELWQR1AA										
ELWQ01AA										
ELWQ11AA										
ELWQ41AA										

Comments: _____ Volume of Alt Standard: _____

Split Ratios: Post I.S. _____

Post F.C. _____

Post C.S. _____

W.B. Temp _____ Post R.S. _____

Figure 4

Example Data Review Checklist

STL Knoxville **Specialty Organics Prep Batch Review/Checklist** **Batch #**_____

SOP: ☐ **KNOX-ID-0008, rev. 2** (water extraction) ☐ **KNOX-ID-0009, rev 2** (solid extraction) ☐ **KNOX-ID-0010, rev. 3** (cleanup) ☐ **KNOX-ID-0013, rev. 1** (PCB extraction)
☐ **KNOX-ID-0014, rev. 0** (Pesticide extraction) ☐ **KNOX-ID-0015, rev. 0** (PAH extraction) ☐ **KNOX-ID-0016, rev. 0** (LR PAH extraction) ☐ **KNOX-ID-0017, rev. 0** (filters & XAD-2)

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Does the batch contain no more than 20 field samples? (Do not count MB, LCS, LCSD, MS, or MSD)					
2. Were the samples extracted by the proper method ?					
3. Were the samples extracted within the required holding times ?					
4. Were all project specific requirements met as noted on the Lot Checklists and Sample Worksheets ?					
5. Were all required QC samples prepared and extracted with the batch at the method required frequency ?					
6. Were MS Run# properly assigned and samples entered on QC tracking Sheet?					
7. Were samples requested properly and request form completed, signed, and dated?					
8. Were the correct weights and volumes entered in Quantims for all samples?					
9. Were the samples properly spiked and the spikes verified ? Were the spike solution ID and spike volumes entered correctly and verified?					
10. Were all cleanup steps properly documented by initials and date?					
11. Was the final volume checked and verified against the supplemental benchsheet and Quantims?					
12. Are the final extracts free of water, precipitates, multiple phases, and color?					
13. Were all appropriate notes and observations recorded on the prep benchsheet and in Quantims?					
14. Were all Quantims batch information completed including; • Batch reviewed • Correct volumes entered • Correct completion date entered • Samples released					
15. Does the prep batch paperwork package contain all required documentation which has been properly and completely filled out, including; • Prep Benchsheet • Supplemental Benchsheet • Standard concentration forms or copies of logbook pages, for all IS, RS, SS, CS, and Native standards. • Lot Checklists for all lots in the batch • Sample worksheets for all samples in the batch in proper order as recorded on tracking sheet					
16. Are all nonconformances documented appropriately and copy included with deliverable?					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

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Figure 4 Continued

Example Data Review Checklist

STL Knoxville Dioxin GC/MS Initial Calibration Data Review / Narrative Checklist
Method: 1613B - KNOX-ID-0004-R1

PFK Date/Time:		Inst:		Win Filename:		Col Perf Filename:	

CS1 Filename	CS2 Filename	CS3 Filename	CS4 Filename	CS5 Filename

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Was the mass resolution documented before beginning the initial calibration?					
2. Was the instrument resolution >10,000 (<100 ppm) on PFK m/z 304.9824 and m/z 380.9760 (at reduced voltage)?					
3. Was the measured exact mass of m/z 380.9760 (PFK) within 5 ppm at reduced accelerating voltage?					
4. Was the Window Defining Mixture analyzed and the MID switchpoints set to encompass the retention time windows of each congener group?					
5. Was the Column Performance solution analyzed and the %Valley ≤25 for separation between 2378-TCDD/F and the closest eluting non-2378 isomer?					
6. Were the five calibration standard solutions, at the concentrations specified in the SOP, analyzed?					
7. Was date/time of analysis verified between analysis header and logbook as correct?					
8. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound, quantitation ions, and formula.					
9. Are %RSD ≤20% for all unlabeled native analytes except 1,2,3,7,8,9-HxCDD and OCDF?					
10. Are %RSD ≤35% for 1,2,3,7,8,9-HxCDD and OCDF and all labeled internal standards ?					
11. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards?					
12. Are the ion abundance ratios for all labeled and unlabeled analytes within the specified control limits?					
13. If manual integrations were performed, are they clearly identified, initialed and dated?					
14. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
15. Does the ICAL folder contain **complete** data in the following order? Data review checklist, a **complete** runlog, Avg. %RSD summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation, and Total RIC, EICP's and manual integration - for window and all standards, in order from low to high standard.					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

ID023R1.doc, 10/16/00

Figure 4 Continued

Example Data Review Checklist

STL Knoxville Dioxin GC/MS Continuing Calibration Review / Narrative Checklist
Method: 1613B - KNOX-ID-0004-R1

Start PFK:		VER Filename:		Win Filename:		Inst:	
End PFK:				Col Perf Filename:		ICAL Date:	

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Was the mass resolution documented at both the beginning and end of the 12 hour shift?					
2. Was the instrument resolution >10,000 (<100 ppm) on PFK m/z 304.9824 and m/z 380.9760 (at reduced voltage)?					
3. Was the measured exact mass of m/z 380.9760 (PFK) within 5 ppm at reduced accelerating voltage?					
4. Was date/time of analysis verified between analysis header and logbook as correct?					
5. Was the Window Defining Mixture analyzed and the MID switchpoints set to encompass the retention time windows of each congener group?					
6. Was the Column Performance solution analyzed and the %Valley ≤25 for separation between 2378-TCDD/F and the closest eluting non-2378 isomer?					
7. Was the continuing calibration performed at the beginning of the 12 hour period after successful mass resolution and GC resolution performance check?					
8. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound, quantitation ions, and formula.					
9. Are the measured RRFs for each compound within the specified control limits in Table 9 for all PCDDs/PCDFs or Table 10 if only TCDD/TCDF are being determined?					
10. Are the relative retention times of all PCDDs/PCDFs and all labeled compounds within the limits specified in Table 8?					
11. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards?					
12. Are the ion abundance ratios for all labeled and unlabeled analytes within the specified control limits?					
13. If manual integrations were performed, are they clearly identified, initialed and dated?					
14. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
15. Does the CCAL folder contain **complete** data in the following order? Data review checklist, a **complete** runlog, CCAL summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation, and Total RIC, EICP's and manual integration - for window and standard.					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

ID023R1.doc, 10/16/00

Figure 4 Continued

Example Data Review Checklist

STL Knoxville Dioxin GC/MS Data Review / Narrative Checklist **LOT #**_____
Method: 1613B - KNOX-ID-0004-R1 **Page 1 of 2**

Batch Number:	

Review Items **A. Initial Calibration**	N/A	Yes	No	Why is data reportable?	2nd Level
1. Was the correct ICAL used for quantitation? (Check 1-2 compounds for batch by manually calculating concentration using the ICAL avg. RF.)					
B. Continuing Calibration					
1. Has a Continuing Calibration Checklist been completed for each analytical batch?					
C. Client Sample AND QC Sample Results					
1. Were all special project requirements met?					
2. Were the header information, prep factors, and dilution factors verified?					
3. Was date/time of analysis verified between analysis header and logbook as correct?					
4. Sample analyses done within preparation and analytical holding time (HT)? *If no, list samples:* _____				• HT expired upon receipt. • * Client requested analysis after HT expired. • Re-extraction done after HT expired. • See Comment no. _____.	
5. Are internal standards within QC limits specified in Table 11 (TCDD/TCDF only Table12)? *If no, list samples and reason (e.g.,* **sur1***):* Sample Reason Sample Reason _____				• * **[sup]** Ion suppression due to matrix. • * **[low]** Low recovery. S/N >10 and EDL<ML. • **[sam]** Not enough sample to re-extract. • **[dil]** Dilution showed acceptable %R. • **[mtx]** Obvious matrix interference. Further cleanup not possible. • * **[unk]** At client's request, data was flagged as estimated and released without further investigation. • **[com]** See Comment no. _____.	
6. Were the following qualitative criteria met for all reported PCDD/Fs: • All 2378 isomers within the RRT limits specified in Table 8 and both ions maximized within ±2 seconds. • All non-2378 isomers within established RT windows and both ions maximized within ±2 seconds. • The ion abundance ratios for all labeled and unlabeled analytes within the specified control limits or within ±10% or the ratio in the CS3 or VER. • All peaks ≥2.5 S/N • No corresponding peak at PCDPE mass.					
7. Were peaks ≥2.5 S/N, which did not meet the above criteria, properly calculated and reported as EMPCs?					
8. Were all positive 2378-TCDF hits confirmed by analysis on DB-225?					
9. Are positive results within calibration range? *If no, list samples:* _____				• OCDD/F or non-2378 exceeded calibration range • Sample extracted at lowest possible volume	
11. If manual integrations were performed, are they clearly identified, initialed and dated?					
12. Final report acceptable? (Results correct, DLs calculated correctly, units correct, IS %R correct, appropriate flags used, dilution factor correct, and extraction/ analysis dates correct.)					
13. Was a narrative prepared and all deviations noted?					

* Such action must be taken in consultation with client.

ID023R1.doc, 10/16/00

Figure 4 Continued

Example Data Review Checklist

STL Knoxville Dioxin GC/MS Data Review / Narrative Checklist **LOT #**_____
Method: 1613B - KNOX-ID-0004-R1 **Page 2 of 2**

D. Preparation/Matrix QC	N/A	Yes	No	Why is data reportable?	2nd Level
1. Have Initial Precision and Recovery (IPR) samples been analyzed? Was the data generated acceptable and all results within the control limits in Table 9 (TCDD/TCDF only Table 10)?					
2. LCS(OPR) done per prep batch and all analytes within the limits specified in Table 9 (TCDD/TCDF only Table 10)? *If no, list LCS(OPR) ID:* _____				• * Reanalysis not possible-insufficient sample. • LCS %R high and affected analyte(s) were <ML in associated samples. • See Comment no._____.	
2. Method blank done per prep batch and method blank or instrument blank analyzed with each sequence?					
3. Method blank internal standard recoveries within QC limits? *If no, list blank ID:* _____				• * Internal standards are high and blank demonstrates that analysis is free of contaminants. • * Sample internal standards OK and there is no analytes >ML in samples associated with blank.	
4. Are all analytes present in the method blank ≤ ML? *If no, list blank ID:* _____				• Sample results are > 20x higher than blank. • * There is no analyte > RL in the samples associated with method blank. • * Reanalysis not possible-insufficient sample	
E. Other					
1. Are all nonconformances documented appropriately and copy included with deliverable?					

Analyst:	Date:	Analyst:	Date:
Comments:		Comments:	

* Such action must be taken in consultation with client.

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Figure 5

Method 1613B - Aqueous Sample Extraction

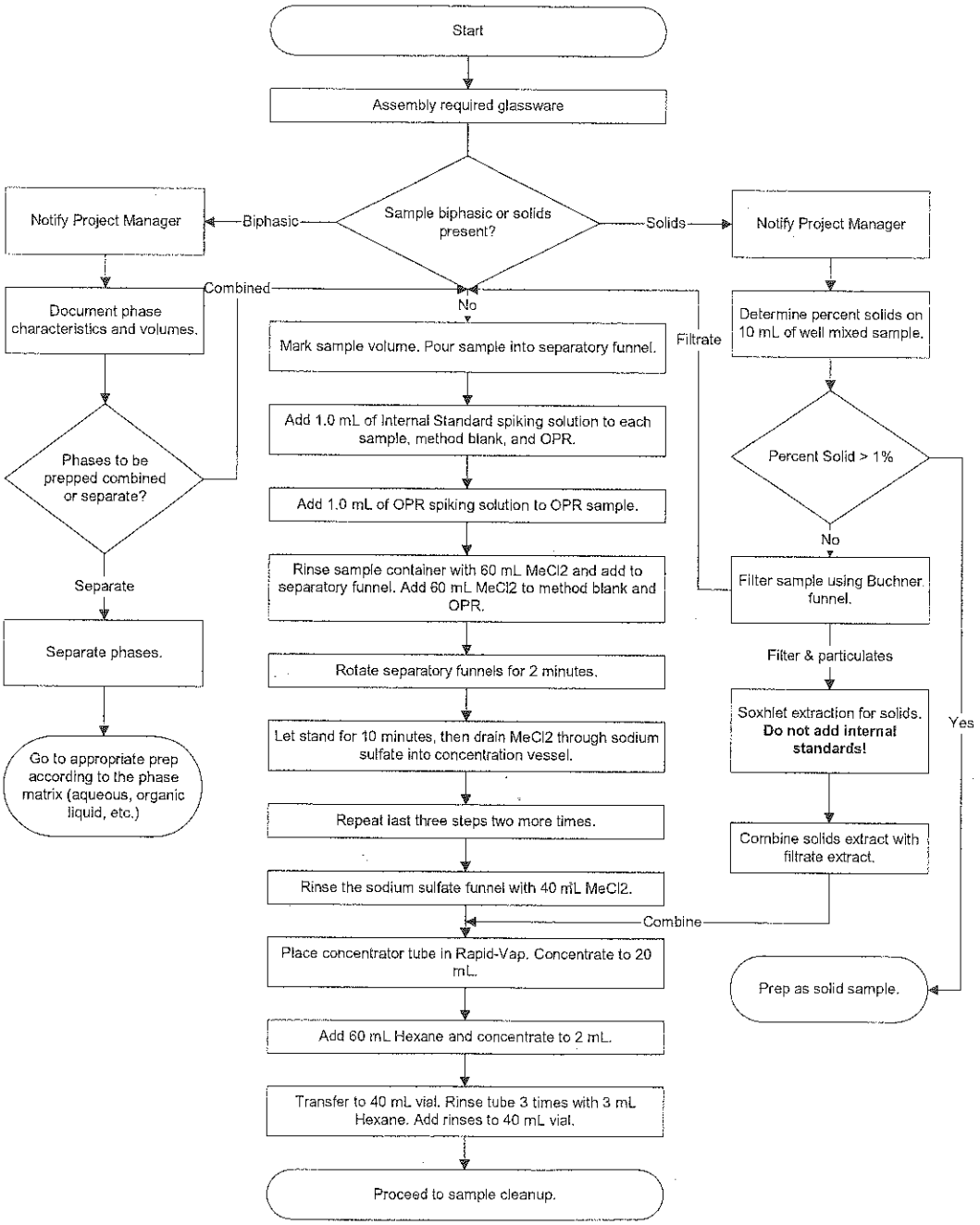


Figure 6

Method 1613B - Solid Sample Extraction

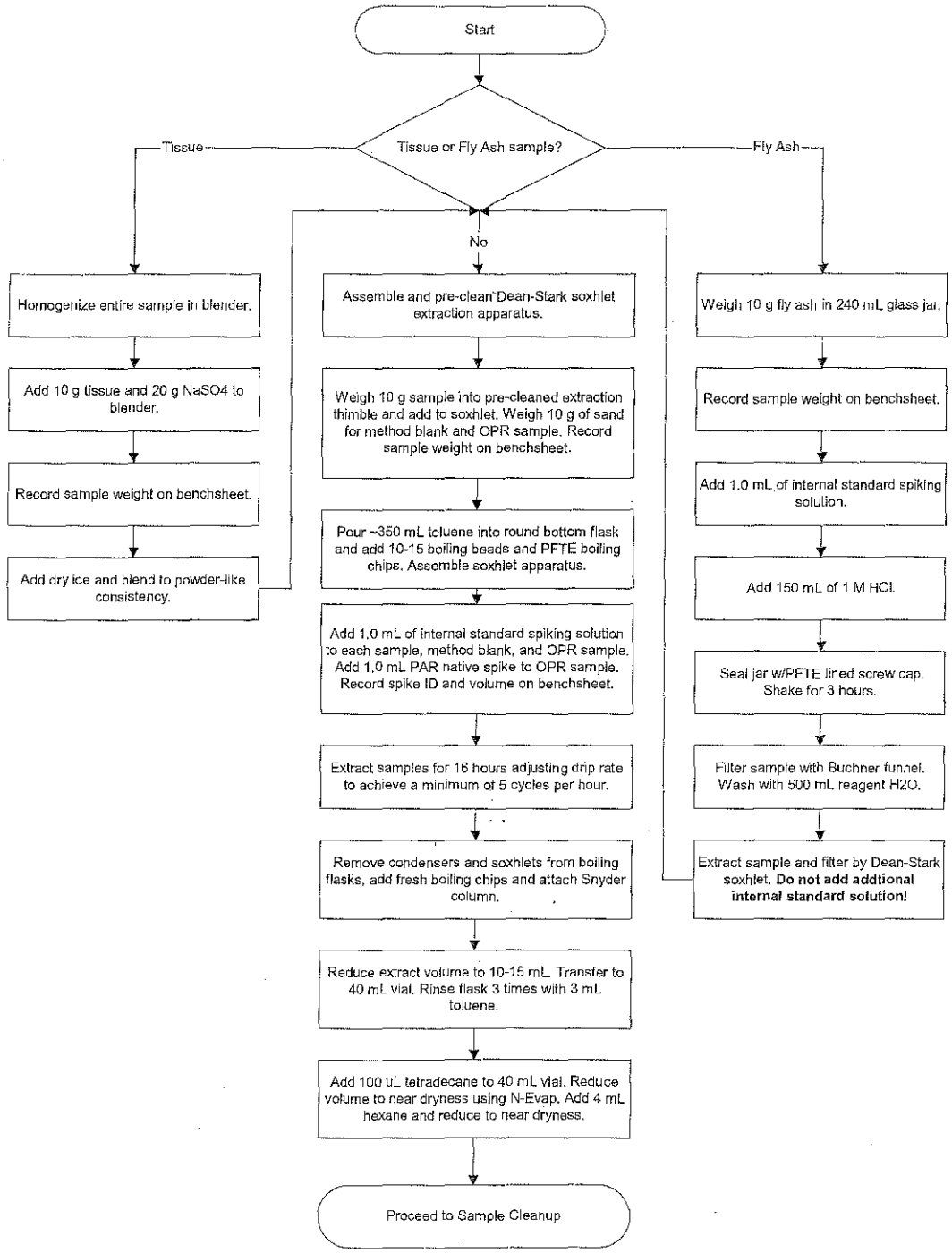


Figure 7

Method 1613B - Sample Cleanup

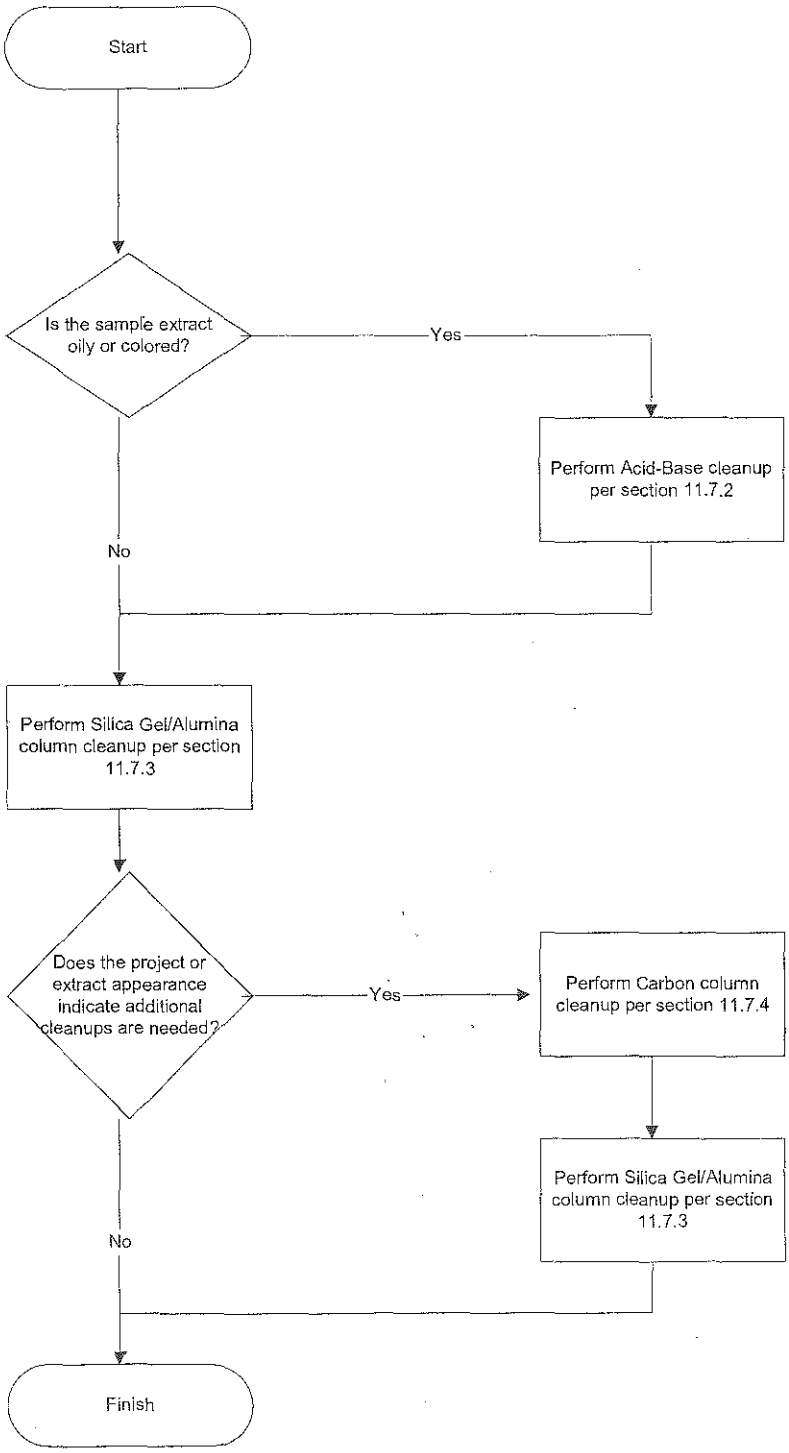
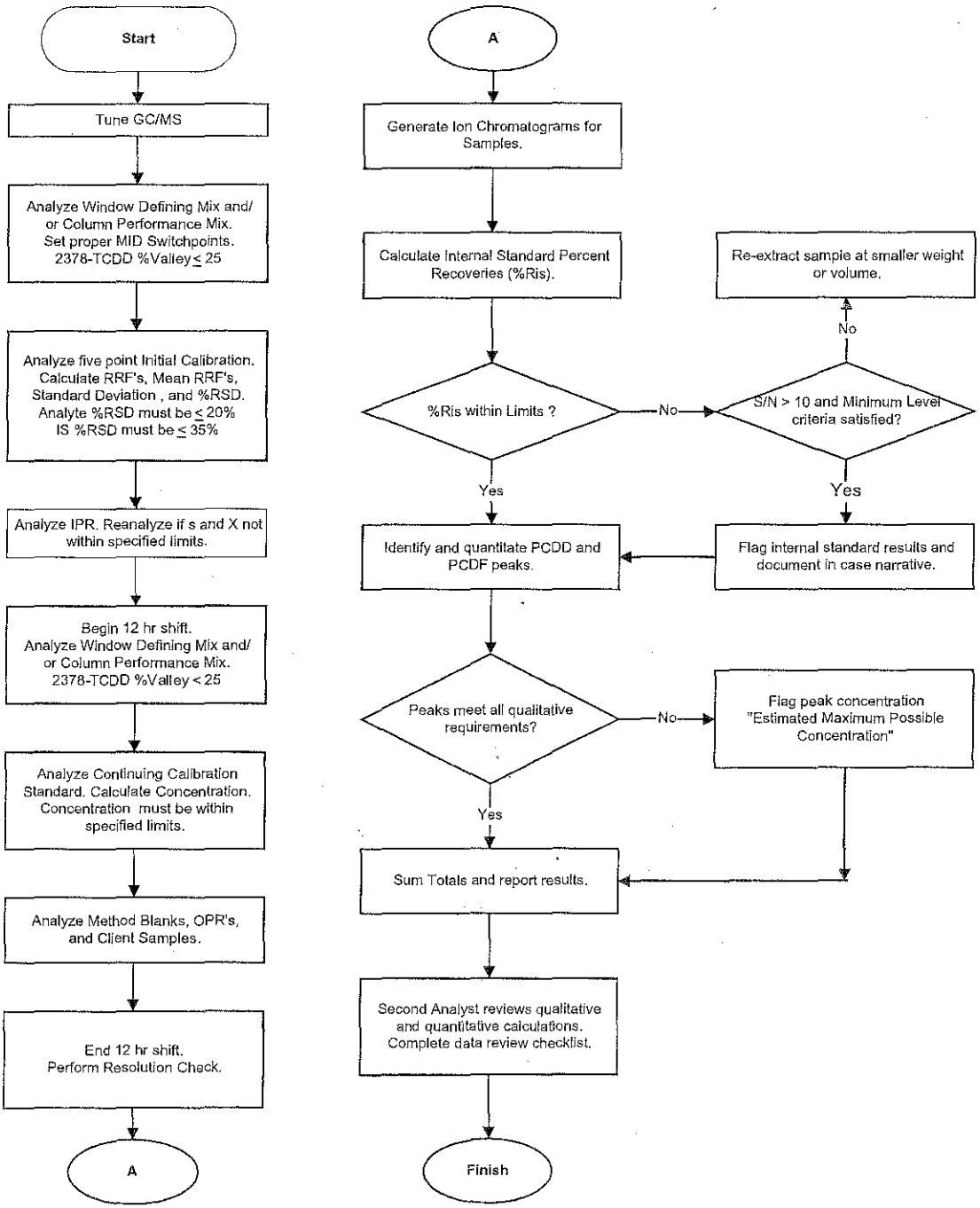


Figure 8

Analysis Of PCDD's and PCDF's by HRGC/HRMS



AK5 042094

ARCADIS GERAGHTY & MILLER

Richard O. Astle
Project Manager

James J. Reid, P.E.
Associate

Quality Assurance Project Plan

Olympic Mills Service Operations Area
AK Steel Property
Middletown Works
Revision: 0-September 2000

Prepared for:
AK Steel Corporation

Prepared by:
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Fax 614 764 1270

Our Ref.:
MI00848.0007.OH001

Date:
29 September 2000

Figures

Appendices

1. Project Description

This document presents a Quality Assurance Project Plan (QAPP) to conduct an investigation of soil, groundwater, and sediment, in the vicinity of Olympic Mills Service (OMS) operations on AK Steel property (Monroe Ditch and Dick's Creek) located in Middletown, Ohio. This QAPP includes a description of the project, project organization and responsibility, quality assurance objectives, sampling and analytical procedures, and data reduction, validation, and reporting requirements. All QA/QC procedures will be structured in accordance with applicable United States Environmental Protection Agency (U.S. EPA) requirements, regulations, guidance and technical standards.

This QAPP was prepared by ARCADIS Geraghty & Miller, Inc. in accordance with the Administrative Order issued by the U.S. EPA in a letter dated August 17, 2000 to Mr. Richard Wardrup, President, of AK Steel Corporation from Mr. Joseph M. Boyle, Chief Enforcement and Compliance Assurance Branch, U.S. EPA, pursuant to Section 7003(a) of the Resource Conservation and Recovery Act (RCRA), 42 U.S.C. 6973(a) and with U.S. EPA Region 5 QAPP policy as presented in U.S. EPA RCRA QAPP instructions.

1.1 Introduction

The purpose of the investigations to be conducted in accordance with this QAPP is to determine the source(s) of polychlorinated biphenyls (PCBs) detected in former groundwater seepage flowing into Monroe Ditch at Areas of Investigation (AOIs) identified within the OMS operations area on AK Steel Property. The following plans (including a description of the sampling network and rationale and standard operating procedures [SOPs]) will be submitted under separate cover:

- Hydrogeologic Investigation Plan
- Soil Investigation Plan

Monroe Ditch and Dick's Creek will be investigated to assess the presence and concentrations of PCBs, polynuclear aromatic hydrocarbons (PAHs) and selected metals. These data will be used to evaluate relative site risks posed to human and ecological receptors, and tissue analysis to evaluate constituent transfer through the food web to ecological receptors. The following plan (including a description of the sampling network and rationale and SOPs) will be submitted under separate cover:

- Sediment Sampling Plan

In addition, an evaluation will be conducted to identify potential alternatives for minimizing the influence the OMS kish pot operations have on groundwater flow and to determine whether reusing the effluent from the current interceptor trench and treatment system in the slag processing operations results in concentrations of PCBs in media (soil, groundwater) or poses a risk of runoff to any surface waters. The results of this evaluation will be used to determine if the existing systems are adequate or if additional measures are necessary. These plans will be submitted under separate cover in the following document:

- Water Use Alternatives in Slag Processing

To ensure that no PCB containing seepage is discharging to surface waters (Monroe Ditch and Dick's Creek) from the OMS operations area, a plan will be developed to inspect the east and west banks of Monroe Ditch, the banks of Dick's Creek adjacent to the closed landfills, and the drainage swales adjacent to closed Landfill 1 for evidence of seepage. The results of the inspections will determine if PCB containing seepage has been eliminated or if additional measures are required. The following plan will be submitted under separate cover:

- Seep Inspection Plan

Finally, a Health & Safety Plan is included in this QAPP (Appendix A) for personnel conducting investigations of the aforementioned media in the OMS operations area, Monroe Ditch and Dick's Creek.

1.2 Site Description

A brief description of the facility, its hydrogeological setting, and associated features is presented in the following sections.

1.2.1 Location

The AK Steel facility is a steel manufacturing plant located in southwestern Ohio in Butler County, in the town of Middletown. The entire plant currently covers an area of approximately 2,600 acres and is involved in various aspects of steel manufacturing and processing. The plant is divided into five areas, including the North Plant, the Melt Area, the Coil Paint Area, the South Plant, and the Slag Processing Area. The

investigation area includes the OMS operations area (located within the Slag Processing Area), Monroe Ditch, and Dick's Creek. These areas are located south of Oxford State Road (Figure 1).

The OMS operations area, where slag processing and recycling activities are performed, is approximately 100 acres in size. Monroe Ditch is located west of the OMS operations area and Dick's Creek is located to the north.

The Monroe Ditch ranges from 5 to 20 feet below land surface of the OMS operations area. Surface water in Monroe Ditch is intermittent and varies with seasonal precipitation. Monroe Ditch flows north along the western boundary of the OMS operations area, then west, then north prior to entering Dick's Creek, which flows east to west.

Dick's Creek flows west and is located north of the OMS operations area and south of Oxford State Road. The surface water flow of Dick's Creek varies with seasonal precipitation, but is typically 2 feet in depth and spans 10 feet in width. The floodplain within the Dick's Creek Channel is approximately 40 feet in width and is bounded by earthen banks having heights of approximately 15 feet (flush with the predominately flat land surface).

1.2.2 Local Geology and Hydrogeology

The AK Steel plant is situated at the intersection of two buried river valleys; the ancestral Great Miami River valley and the ancestral Todds Fork River valley, which were deposited as glacial outwash, till and lake deposits form Illinoisan and Wisconsin glaciation. Currently, the Great Miami River occupies the western edge of the ancestral Miami River valley. Dick's Creek, a tributary to the Great Miami River, is the major stream of the ancestral Todds Fork Valley. Dick's Creek drains into the Great Miami River approximately 2 miles west of the plant (Geraghty & Miller, Inc. 1989).

Previous site-wide hydrogeologic investigations indicate that groundwater beneath the site occurs in three aquifers, which are designated as the upper, intermediate, and lower aquifers. In most locations, these aquifers are confined by silt and clay till, or clay-confining units, resulting in limited hydraulic communication between the aquifers beneath the AK Steel facility.

The upper aquifer is present in the southern part of the AK Steel property, including the OMS operations area, at depths ranging from 5 to 30 feet below land surface (ft

bls). The upper aquifer ranges in thickness from 5 to 10 ft, with a maximum thickness of 15 ft, and typically consists of brown, well sorted, fine to medium-grained sand with some very fine sand, silt and gravel. In some cases, the upper aquifer may contain lenses of silt and clay. Upper and intermediate aquifer wells installed in the vicinity of the OMS operations area indicate that groundwater flow is north towards Dick's Creek. Site-wide hydrogeologic data indicates that Dick's Creek acts as line sink for the upper aquifer.

The intermediate aquifer is present beneath the OMS operations area, and is separated from the upper aquifer by a silt and clay till or confining unit. The intermediate aquifer is composed of fine to coarse sand and gravel with traces of silt; however, the composition of the intermediate aquifer varies greatly across the site. The saturated thickness of the intermediate aquifer ranges from 2 ft to 14 ft in the OMS operations area, and generally thickens from south to north.

The lower (sole-source) aquifer is not present in the vicinity of the OMS operations area. Instead, shale and limestone bedrock underlie the intermediate aquifer. The base of the intermediate aquifer is comprised of silt and clay, which limits the movement of groundwater between bedrock and the intermediate aquifer.

1.2.3 Surrounding Land Use

The OMS operations area is used to process and recycle slag generated from steel making operations in the main plant. A railroad and farmland are located south of the OMS operations area. Dick's Creek and commercial property are located north of the OMS operations area. Steel processing activities are performed east of the OMS operations area. Monroe Ditch and closed Landfill 1 are located west of the OMS operations area. Another closed landfill is located northwest of the OMS operations area between Monroe Ditch and Dick's Creek. These solid waste landfills were closed by November 1980. According to AK Steel, no sources of PCBs are believed to be present on property outside the OMS operations area. Figure 2 provides a site layout of the OMS operations area.

1.3 Site/Facility History

1.3.1 General History

The OMS operations area was used as farmland until 1965, when McGraw Construction began slag processing and recycling activities. In 1985, International

Mills Service, Inc. (IMS) purchased McGraw and took over these operations. OMS took over the slag processing and recycling activities in 2000. The site is currently used for slag processing and recycling activities.

Three ponds were present along the southern boundary of the OMS operations area (Figure 2). These ponds were found to contain PCBs and were used to gravity separate waste oils from the Middletown Works during the 1960s and early 1970s. This practice was terminated in 1974 with the construction of the No. 4 Oil Recovery Plant. From 1974 forward, the oils that had been taken to these ponds for separation were then taken to the No. 4 Oil Recovery Plant where the separation was conducted in steel tanks. It appears that some hydraulic oils containing PCBs were taken to these three ponds prior to 1974.

In preparation for closing these three ponds in 1980, the oil, water, and bottom solids were sampled. The oils, waters and sludges were non-hazardous, but the sampling results showed that the solids and oil phases of all 3 ponds had PCB concentrations in the 100 parts per million (ppm) range. The water phase showed very low levels of PCBs. AK Steel contracted with CECOS to manage the closure of the ponds. The closure activity took place around 1983.

Closure activities included the removal of water from the ponds. This water was treated through carbon filtration and then trucked to North Terminal Treatment Plant for further treatment and discharge to the Great Miami River. After the water was removed from the ponds and treated, the oil and solids were solidified with lime. The solidified material was transported to the Toxic Substances Control Act (TSCA)-approved landfill until all samples contained less than 2 parts per million (ppm) PCBs. The ponds were then backfilled with brick and rubble (construction and demolition debris), capped with at least two feet of native clay, and seeded.

Historical placement of solid waste occurred in the vicinity of the OMS operations area. Currently, Monroe Ditch bisects three closed solid waste landfills. The landfills were closed during November 1980.

Prior to the early 1960's, Dick's Creek was a meandering stream. Dick's Creek was then constructed as a straight channel under the direction of the Miami Conservancy District to provide flood protection in Dick's Creek watershed.

1.3.2 Past Data Collection Activities

On October 31, 1997, while working in Dick's Creek near the AK Steel facility in Middletown, Ohio, the Ohio Environmental Protection Agency (Ohio EPA) observed a white substance coming from Monroe Ditch, which flows intermittently to Dick's Creek. Ohio EPA collected a sample of the substance for analyses during November 1997 and traced the discharge back to a seep on the east bank of Monroe Ditch. The substance was determined to be coming from the property, which IMS operated for slag processing and recycling. Ohio EPA then sampled multiple sites along the Monroe Ditch and seepage into Monroe Ditch. Analyses of the seep samples indicated the presence of PCBs. In a letter to Mr. M. T. Adams of AK Steel and Mr. Jerry Piccioni of IMS (now OMS) dated December 5, 1997 the Ohio EPA notified AK Steel of the results and ordered that the discharge be ceased (Ohio EPA, 1997).

On December 15, 1997, Geraghty & Miller (now ARCADIS Geraghty & Miller), acting on behalf of AK Steel, prepared a plan for the investigation and remediation of groundwater seepage into the Monroe Ditch Area. The proposed plan was two fold: 1) implement interim measures to stop current seepage to Monroe Ditch and 2) conduct a phased investigation to determine the source and extent of PCBs. The interim measures were implemented in December 1997 and January 1998, and consisted of installing a trench and sump (constructed parallel to Monroe Ditch) that intercepted water before it could discharge as a seep to the ditch. Pre-design investigations and installation descriptions are presented in Preliminary Plan for Investigation and Remediation, Monroe Ditch Area, AK Steel property, Middletown, Ohio (ARCADIS Geraghty & Miller, 1998).

During low-water periods (late 1998) in Monroe Ditch, seepage at a rate of approximately one gallon per hour was occasionally observed flowing into Monroe Ditch from below the bottom evaluation of the trench line. To eliminate this low-flow seepage the interception trench was extended 100 feet south, and a lateral interception trench was installed west and at a lower elevation than the original interception trench. The trench extension was constructed in the same manner presented in the Preliminary Plan for Investigation and Remediation (ARCADIS Geraghty & Miller, 1998) for the original trench. Since the installation of the extension and lateral trench during January 1999, no additional seeps have been observed.

ARCADIS Geraghty & Miller conducted interviews, a file review, and site visits to determine the potential source(s) of PCBs in groundwater. Based on the results of these activities the following Areas of Investigation (AOIs) have been identified:

- Transformers;
- Former Oil Separator Ponds;
- Former Drainage Path;
- Compressor Building;
- Oil Storage Area;
- Air Dump;
- Mill Scale Area 1;
- Mill Scale Area 2; and
- Mill Scale Area 3.

These AOIs were investigated under the Ohio Voluntary Action Program (Ohio VAP) in accordance with Ohio Administrative Code (OAC) 3745-300-07. Results of this initial investigation are summarized in the *Monroe Ditch Investigation First Interim Report, AK Steel Property, Monroe Ditch Area, Middletown, Ohio* by ARCADIS Geraghty & Miller, prepared for AK Steel Corporation, dated July 15, 1999.

1.3.3 Current Status

Currently, this QAPP, a Hydrogeologic Investigation Plan, a Soil Investigation Plan, a Sediment Sampling Plan, a Seep Inspection Plan, and a Water Use Alternatives Plan have been submitted to the U.S. EPA in response to the Administrative Order issued by the U.S. EPA in a letter dated August 17, 2000 pursuant to Section 7003(a) of the RCRA, 42 U.S.C. 6973(a). Further delineation investigations of PCBs in soil and groundwater (as described in the Hydrogeologic Investigation Plan and the Soil Investigation) are underway.

1.4 Project Objectives and Intended Data Usages

The project objectives will be to ensure that sufficient information will be gathered in the AOIs to determine the source(s) of PCBs detected in groundwater in the OMS operations area, the nature and extent of PCBs in soil and groundwater. Sufficient

information will also be collected to evaluate sediment within Monroe Ditch and Dick's Creek to determine the nature and extent of PCBs, PAHs, and selected metals. The sampling network, rationale, and methodology for the collection and evaluation of these data are summarized in the following plans, which will be submitted under separate cover:

- Hydrogeologic Investigation Plan
- PCB Source Identification and Removal Plan
- Sediment Sampling Plan

Each of these plans includes a list of target parameters (including a list of field and laboratory parameters), sampling locations, sampling rationale, and a project schedule.

1.5 Project Schedule

A schedule for each investigation phase is presented within individual sampling plans.

2. Project Organization and Responsibility

ARCADIS Geraghty & Miller/AK Steel has responsibility for all phases of the investigation. ARCADIS Geraghty & Miller/AK Steel will perform the field investigation, prepare the Report, and perform any subsequent studies. ARCADIS Geraghty & Miller/AK Steel will provide project management. Specific individuals will be designated upon implementation of the project. An organization chart is presented in Figure 3.

2.1 Laboratory Responsibilities

The following provides a list of laboratories responsible for the analyses of samples. Each laboratory Project Manager, Operations Manager, and Quality Assurance Officer and their responsibilities are also listed.

The laboratory tasked with responsibility for alkylated (NOAA/EMAP) PAH analyses is:

B&B Laboratories
1902 Pinon
College Station, TX 77845
Phone: 979.693.3446

Quality Assurance Officer: Sue McDonald

The laboratory tasked with the responsibility for PCB homologue and aroclor analyses is:

Severn Trent Laboratories (STL) Savannah
5102 LaRoche Avenue
Savannah, GA 31404
Phone: 912.351.3673

Quality Assurance Officer: Kirsten McCracken

Another laboratory tasked with the responsibility for PCB aroclor analyses is:

Test America Incorporated
Dayton Division
3601 South Dixie Drive

Dayton, Ohio 45439

Quality Assurance Officer: Jim Davis

The laboratory tasked with the responsibility for target metals is:

Columbia Analytical Services
1317 South 13th Avenue
Kelso, WA 98626
Phone: 360.577.7222

Quality Assurance Officer: Lee Wolf

The laboratory tasked with the responsibility for geotechnical analysis:

Thompson Engineering
3707 Cottage Hill Road
Mobile, AL 36609
Phone: 334.666.2443

Quality Assurance Officer: Dale Nobile

Laboratory Project Manager

The laboratory project manager will report directly to the ARCADIS Geraghty & Miller project manager and will be responsible for the following:

- Ensuring all resources of the laboratory is available on an as-required basis.
- Overseeing production and final review of analytical reports.

Laboratory Operations Manager

The laboratory operations manager will report to the [laboratory] Project Manager and will be responsible for:

- Coordinating laboratory analyses.
- Supervising in-house chain-of-custody.

- Scheduling sample analyses.
- Overseeing data review.
- Overseeing preparation of analytical reports.
- Approving final analytical reports prior to submission to ARCADIS Geraghty & Miller/AK Steel.

Laboratory Quality Assurance Officer

The laboratory QA officer has the overall responsibility for data after it leaves the laboratory. The laboratory QA officer will be independent of the laboratory but will communicate data issues through the laboratory project manager. In addition, the laboratory QA officer will:

- Oversee laboratory QA.
- Oversee QA/QC documentation.
- Conduct detailed data review.
- Determine whether to implement laboratory corrective actions, if required.
- Define appropriate laboratory QA procedures.
- Prepare laboratory SOPs.
- Sign the title page of the QAPP.

Final responsibility for project quality rests with ARCADIS Geraghty & Miller's Project Manager. Independent QA will be provided by the laboratory Project Manager and QA Officer prior to release of all data to ARCADIS Geraghty & Miller/AK Steel.

Laboratory Sample Custodian

The laboratory sample custodian will report to the laboratory operations manager. Responsibilities of the laboratory sample custodian will include:

- Receiving and inspecting the incoming sample containers.
- Recording the condition of the incoming sample containers.
- Signing appropriate documents.
- Verifying chain-of-custody.
- Notifying laboratory manager and laboratory supervisor of sample receipt and inspection.
- Assigning a unique identification number and customer number, and entering each into the sample-receiving log.
- With the help of the laboratory manager, initiating transfer of the samples to appropriate lab sections.
- Controlling and monitoring access/storage of samples and extracts.

Laboratory Technical Staff

The laboratory technical staff will be responsible for sample analyses and identification of corrective actions. The staff will report directly to the laboratory operations manager.

2.2 Field Responsibilities

The ARCADIS Geraghty & Miller field team leader will support the AK Steel project manager. He/she is responsible for leading and coordinating the day-to-day activities of the various resource specialists under his/her supervision. Specific field team leader responsibilities include:

- Provision of day-to-day coordination with the AK Steel project manager on technical issues in specific areas of expertise;
- Developing and implementing field-related work plans, assurance of schedule compliance, and adherence to management-developed study requirements;

- Coordinating and managing field staff including sampling and drilling, and supervising field laboratory staff;
- Implementing QC for technical data provided by the field staff including field measurement data;
- Adhering to work schedules provided by the project manager;
- Authoring, writing, and approving of text and graphics required for field team efforts;
- Coordinating and overseeing technical efforts of subcontractors assisting the field team;
- Identifying problems at the field team level, resolving difficulties in consultation with the AK Steel and ARCADIS Geraghty & Miller project managers, implementing and documenting corrective action procedures, and provisions of communication between team and upper management; and
- Participating in preparation of the final report.

ARCADIS Geraghty & Miller Field Technical Staff

The technical staff for this project will be drawn from ARCADIS Geraghty & Miller's pool of corporate resources. The technical staff will be utilized to gather and analyze data and to prepare various task reports and support materials. All of the designated technical team members are experienced professionals who possess the degree of specialization and technical competence to effectively and efficiently perform the required work.

3. Quality Assurance Objectives

The overall QA objective for this project is to develop and implement procedures for field sampling, laboratory analysis, chain-of-custody, and reporting that will provide results that are of known and acceptable quality. This section will provide in greater detail specific project objectives and intended data usages mentioned in Section 1 of this QAPP. Specific procedures for sampling, chain-of-custody, laboratory instrument calibration, laboratory analysis, reporting of data, internal QC, audits, preventive maintenance of field equipment, and corrective action are described in other sections of this QAPP.

3.1 Precision

Precision is the degree of mutual agreement of independent measurements as a result of repeated application of a process under specific conditions. Precision is concerned with the closeness of results during repeated analysis of the same sample. Precision is addressed by calculating the relative percent differences (RPD) for each pair of duplicate analyses using the following equation:

$$\%\text{RPD} = \frac{(S - D)}{(S + D)/2} \times 100$$

where:

S = First sample value

D = Second sample value

Precision objectives for each analytical method in terms of the RPD of duplicate measurements have been specified for laboratory measurements.

The following QC samples may be used to evaluate precision in the laboratory:

- Laboratory duplicates,
- Reagent water blank spike duplicates, or
- Matrix spike duplicates.

The following QC samples may be used to evaluate precision in the field:

- Field duplicates (which are also used to determine precision for laboratory analyses).

3.2 Accuracy

Accuracy is the degree of agreement of a measured value with the true or expected value. Accuracy objectives for each analytical method in terms of the percent recovery (%R) from analysis of samples of known analyte concentration are presented in the laboratory QAP. Accuracy is assessed by using the following equation:

$$\%R = \frac{A - B}{C} \times 100$$

where:

A = The analyte concentration determined experimentally from the spiked sample;

B = The background level determined by a separate analysis of the unspiked sample; and

C = The amount of the spike added.

The following QC samples will be analyzed to evaluate accuracy in laboratory measurements:

- Laboratory control samples,
- Matrix spikes, or
- Reagent water blank spikes.

3.2.1 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that is expected under the conditions of the measurement. At least 95 percent of all samples analyzed by the laboratory must be valid to be considered complete. Completeness is assessed using the following equation:

$$C = \frac{\text{Valid Data Obtained}}{\text{Total Data Planned}} \times 100$$

3.3 Representativeness

Representativeness expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. As such, representativeness describes whether samples collected, or the aliquot selected by the laboratory for analysis, are sufficient in number, type, location, frequency, and size to be characteristic of the substance analyzed.

Representativeness is a qualitative parameter that is dependent upon the proper design of the sampling program and proper laboratory protocol. The sampling network for this project was designed to provide data representative of site conditions. Representativeness will be met by ensuring that work specifications are followed, proper sampling techniques are used, and proper analytical procedures are followed.

3.4 Comparability

Comparability expresses the confidence with which one data set can be compared with another. The extent to which existing and planned analytical data will be comparable depends on the similarity of sampling and analytical methods. The procedures used to obtain the planned analytical data, as documented in the sampling SOPs and each laboratory QAPP are expected to provide comparable data. However, it must be recognized that for different data sets to be truly comparable, all aspects of the collection and measurement process should be identical. Some of the parameters that should be consistent to ensure comparability include the following items:

- Samples must be from the same source,
- Samples must be collected in the same or similar manner,
- Samples must be preserved in the same manner,
- Samples must be prepared and analyzed by the same method,

- Data must be reported in the same units, and
- Data from each set must be of comparable quality.

3.5 Required Detection Limits

Detection limits have been specified for soil and aqueous matrices according to the analytical methodology. The laboratory is required to have conducted, and have a record of, a baseline detection limit study for all methods. This study is required to be periodically updated and/or revised when changes in instrumentation or methods occur within the laboratory. With the exception of demonstrated matrix interferences or sample dilution/concentration requirements, the laboratory is required at any time to be able to demonstrate the ability to achieve the detection limits stated in the analytical reports generated by the analysis of investigative samples. Analytical methodology and method detection limits requirements are presented in each sampling plan for each parameter to be analyzed.

In the laboratory data packages, the laboratory must use reporting limits at or below the limits specified, unless the specified detection limits are not obtainable by the laboratory due to matrix interferences or high parameter concentrations requiring sample dilution.

4. Sampling Procedures

This section presents the field data collection methods and procedures to be implemented during the planned investigations. The procedures to be used during the investigation were chosen for their ability to provide data representative of site conditions, compatibility with analytical considerations, practicality, and simplicity. SOPs for sediment, soil and groundwater sampling are provided in their respective sampling plans that will be submitted to the U.S. EPA as separate documents.

4.1 Sample Containers, Preservatives, and Volume Requirements

The required sample containers, preservatives, and volumes for analyses of PCBs, PAHs, and target metals will be collected in accordance with the respective laboratory QAPP. The volume of sample collected must be sufficient to perform the required analyses with an additional amount for QC needs (matrix spikes, duplicates, etc.). All sample containers used for the collection of samples will be pre-cleaned by the manufacturer or by the laboratory supplying the sample bottles, as appropriate.

4.2 Equipment Decontamination

Equipment decontamination procedures are provided in each sampling plan. The laboratory detergent used for equipment decontamination will be a standard brand of phosphorus-free laboratory detergent. The laboratory detergent used should not contain the analytes of concern. Distilled or deionized water will be used during cleaning procedures for field equipment. Laboratory detergent and rinse waters used to clean equipment shall not be reused.

Nondedicated sampling equipment (stainless steel bowls, spoons, scoops, spades, augers, glass mixing bowls, glass measuring cups, etc.) will be decontaminated using the appropriate procedures included in each sampling plan. All sampling equipment decontamination will be performed in the field. When possible, equipment will be decontaminated in batches at a central staging area. All non-disposable equipment will be decontaminated prior to use, following use, between each sampling location, and prior to storage.

4.3 Sample Packaging and Shipping Procedures

Samples will be maintained on ice at 4°C (+/- 2°C) under proper chain-of-custody until shipped via overnight delivery by common carrier or delivered in person to the

laboratory. Aqueous samples will be shipped or delivered in person to the laboratory within 48 hours after collection.

All samples will be packed in ice chests along with proper chain-of-custody forms. All coolers will be sealed with packing tape and custody seals will be attached. Glass sample bottles will be wrapped in plastic bubble pack for protection from breakage. Other standard packing materials may also be used. Sample containers will be arranged to minimize movement when shipping to prevent contact between containers.

4.4 Field Records

All field activities will be recorded in the field at the time of the activity. Several different types of records may be created during the sampling event. All records will be prepared in permanent ink, will be dated and signed by the author, and any errors will be corrected by drawing a single line through the error and initialing and dating the error. All records will be maintained in the project files as a permanent record.

Project field activities will be documented on daily work description logs. Subsurface lithology will be documented on boring logs and the installation of each monitoring well will be described on a well construction log. Standard log sheets for soil and groundwater sampling will be completed, as appropriate, for each sample collected. These logs will be completed as samples are collected. Field notes will be signed at the end of each day. All information will be recorded in indelible ink.

4.5 Sample Identification

Sample labels are necessary to identify the samples. The labels shall be affixed to the sample container (not the caps) prior to or at the time of sampling. Pertinent information on the labels shall be filled out in water-proof ink at the time of collection and will include the following information:

- Sample number/identification code;
- Name (initials) of collector;
- Date and time of collection;
- Project title and/or project number;

- ARCADIS Geraghty & Miller;
- Required analyses;
- Analysis method;
- Sample matrix; and
- Preservative.

After collection, all samples will be handled as little as possible. Field personnel will use extreme care to maintain the integrity of the samples. If samples are placed in a cooler with ice, personnel will package the ice so that melted ice will not leak into the sample containers or cause cross contamination.

5. Custody Procedures

Sample custody is a vital aspect of sampling procedures because data generated during sampling activities may be used as evidence in a court of law. The samples must be traceable from the time of sample collection, through sample analysis, data generation, and report preparation.

5.1 Sample Container Custody

All containers will be shipped from the supplier to the ARCADIS Geraghty & Miller office or a location designated by the ARCADIS Geraghty & Miller Project Manager by common carrier in sealed containers. The supplier will include a shipping form or laboratory chain-of-custody listing all containers shipped and the purpose of each container. It is ARCADIS Geraghty & Miller policy that all containers are considered to be in the custody of the supplier until the sample containers are received by ARCADIS Geraghty & Miller. Upon receipt, sample containers will be checked to determine if any breakage occurred during shipment. The containers will be maintained in the custody of the receiver in a clean, secure area until they are used for sample collection. Once samples have been collected, they will be maintained in the custody of the sampling personnel. The procedure for maintaining and documenting chain-of-custody in the field will be as follows:

1. The sample label that is affixed to the container will be inspected to confirm that all of the required information has been provided.

2. The sample container will be sealed in a zip-lock plastic bag or wrapped in bubble pack, and packed in a cooler chest in a manner that will minimize movement. All samples will be cooled with wet ice.

3. For each cooler chest that is sent to the laboratory, a Chain-of-Custody Record will be completed. All information on the Chain-of-Custody Record and the sample container labels will be checked against field records and the samples will be recounted.

4. If a commercial courier service (e.g., FedEx) is being used to transport the samples to the laboratory, the Chain-of-Custody Record will be signed by a member of the field team, and a copy of the Record will be retained by the field team. The remaining copy(ies) of the Record will be sealed in a zip-lock plastic bag and placed in the cooler chest with the samples. The cooler chest will be sealed with

packaging tape and two custody seals that have been signed and dated by a member of the field team. Because commercial couriers will not sign chain-of-custody forms, the package routing documentation maintained by the courier service during shipping serves as chain-of-custody documentation for the samples.

All laboratory analysts and technicians must follow chain-of-custody protocols described in the respective laboratory's QAPP.

5.2 Data Archiving and Final Evidence File

A Final Evidence File will be developed for data generated during the hydrogeological investigation and will include the following items: all reports, field notes, laboratory reports, signed chain-of-custody forms, sampling procedures, and any other pertinent documents. These items shall be stored in a central location with access limited to select project personnel. The file custodian will be the ARCADIS Geraghty & Miller Project Manager or his designee.

6. Calibration Procedures and Frequency

This section describes procedures for calibrating all field and laboratory instruments used for conducting field measurements and laboratory analyses.

6.1 Field Instrument Calibration

Instruments and equipment used to gather, generate, or measure environmental data will be calibrated with sufficient frequency and in such a manner that accuracy and reproducibility of results are consistent with the manufacturer's specifications.

Equipment to be used during the field sampling will be examined prior to conducting the field investigation to certify that it is in operating condition. This includes checking the manufacturer's operating manual and the instructions for each instrument to ensure that all maintenance requirements are being observed.

Calibration of field instruments is governed by the manufacturers' specific SOP for the applicable field analysis method, and such procedures take precedence over the SOPs presented in each individual work plan.

Calibration and calibration checks of field instruments will be in accordance with the procedures described in appropriate SOPs presented in each individual work plan. Calibration will be performed at the intervals specified by the manufacturer, or more frequently if conditions dictate. In the event that an internally calibrated field instrument fails to meet calibration/check-out procedures, it will be returned to the manufacturer for service and an alternate back-up instrument will be made available.

6.2 Laboratory Instrument Calibration

The calibration procedures and calibration frequency employed by the laboratory will be in accordance with the analytical methods specified in the respective laboratory's QAPP. Records of instrument calibration, repairs, and replacement activities will be maintained. These records will be filed at the location where the work is performed and will be subject to QA audit at any time.

7. Analytical Procedures

The laboratories (including the laboratory address and phone number) designated to perform sample analyses are summarized in Section 2.4 of this QAPP. Analytical methods (SOPS) for each parameter to be analyzed by the laboratory are presented in each sampling plan (submitted under separate cover). Field measurements will be performed in accordance with the SOPs presented in each sampling plan (submitted under separate cover).

8. Internal Quality Control Checks

8.1 Field Quality Control Samples

Field QC samples are necessary to monitor both field and laboratory performance. Field QC samples provide a means of checking the validity of the sample results. These data will be periodically examined to determine if any problems are evident with specific types of media samples or with the procedures used by the subcontracted laboratory. Field QC samples to be collected during sampling activities include duplicate samples (aqueous only) and rinseate blanks. The frequency of field quality control sample collection is described in greater detail in each specific work plan (submitted under separate cover).

8.1.1 Duplicate Samples

The precision of aqueous sample collection techniques will be monitored through the collection and analyses of a field duplicate sample. This type of sample also may serve as a rough estimate of the laboratory analytical precision based on the sample homogeneity. Duplicate samples are collected by equally dividing the sample removed from an aqueous sample source, then placing the aliquots into separate, but identical, sample containers. This process will be repeated until each sample container is properly filled, thus resulting in two samples.

8.1.2 Rinseate Samples

The effectiveness of personnel sample-handling techniques may be monitored by submitting preserved equipment rinseate blank samples for laboratory analysis. These blank samples will be prepared by field personnel and treated in the same manner as actual samples. Rinseate blanks are collected from pouring distilled water so that contact with the field sampling apparatus (coring device, spoons or bowls etc.) is made after it has been decontaminated. That water is collected in appropriate sample containers, preserved in the same manner as the field samples, and analyzed for the parameters/analytes of investigation. Appropriate sample containers for each analyte group must be used. These blanks will be appropriately labeled and documented in field records. These blanks will be stored, transported, and analyzed with the samples.

8.2 Laboratory Quality Control

Laboratories are required to demonstrate their ability to produce acceptable results using the methods selected by the generation of acceptable QC data. Analytical data is evaluated by the laboratory prior to submittal based on internal reviews of the QC data. Internal laboratory QC procedures used to assess laboratory performance are specified in the respective laboratory SOPs (Appendix B).

Internal QC checks performed during this project to assess sampling procedures and laboratory performance include preparation and submittal of duplicate samples (aqueous only), rinseate blanks and field blanks for analysis of all parameters of investigation.

8.2.1 Laboratory Internal Quality Assurance/Quality Control Program

Analytical QC checks are performed in each laboratory. These procedures are based upon U.S. EPA analytical methods guidance and generally accepted standards of good laboratory practice. Key components of the laboratory's QA/QC Program are discussed in the respective laboratory QAPPs.

9. Data Reduction, Validation And Reporting

9.1 Data Reduction

Data reduction is the process of converting analytical data from electronic form or instrument form into digital form and correcting for all sample weight, dilution factors, and percent solids calculations that may be applicable. This process is performed in the field and in the laboratory.

Raw data from field measurements and sample collection activities are recorded in the field records and on applicable field log sheets. Instrument readings are recorded directly into the field records. Recorded field data will be checked by the ARCADIS Geraghty & Miller Project Manager or designee during data validation of field data.

Raw data from analytical laboratory measurements may or may not be generated by digital read out instruments. In addition, due to dilution and concentration factors often developed during the analysis of the sample, careful data reduction is required to convert raw data to useable digital analytical data. All data reductions will be performed according procedures presented in the respective laboratories QAPPs.

9.2 Reporting Requirements

For analytical data quality to be adequately assessed, it is imperative that expected reporting levels are communicated to the laboratories. The laboratories must submit, in addition to the analytical results, all supporting QC data required for effective validation of the analytical data.

If increased defensibility of the laboratories reports data is required, additional documentation of analytical QC data should be available upon request to the laboratories to support validation conclusions and data usability determinations.

All the laboratories data reports will consist of sample results plus the QA/QC data specified below. The following are general requirements for each sample analyzed by the laboratories:

- The results of each analysis;
- The list of the parameters of investigation;

- The method of analysis and the detection limit for each analyte;
- Dates of sample collection, receipt, preparation/extraction, and analysis;
- Copy of the chain-of-custody forms signed by the laboratories sample custodian;
- A narrative summarizing any QA/QC deviances and the corrective action taken; and
- A master list relating laboratories ID to sample ID.

The list below describes the information to be provided for all inorganic analyses (where applicable):

- Results of laboratories method blank samples;
- Results of the batch specific laboratories duplicate analysis; or
- Results of analysis of a batch specific matrix spike or reagent water spike with the compound or element of investigation, the expected value, percent recovery, control limits, and source of control limits.

The list below describes the information to be provided for all the organic analyses performed on a gas chromatograph (GC) (where applicable):

- Results of method blanks and trip blanks, water blanks and/or extraction blanks;
- Results of matrix spike/matrix spike duplicate, control limits, expected value, RPD, and %R; and,
- Results of surrogates spikes, the expected value, control limits, and %R.

9.3 Data Validation

Data validation is a systematic process for reviewing a body of assembled analytical results against a set of criteria to determine if the data is adequate for its intended use. Data validation involves 1) data editing, 2) data screening and checking, 3) data auditing and verification, 4) data certification, and 5) final data review and informed decision-making whereby data is accepted, qualified or rejected.

The data validation procedures employed for this project will include an evaluation of the field data package and an evaluation of the laboratories analytical data packages. The field data package validation procedure will include but not be limited to the following tasks:

- A review of field data contained in sampling logs for accuracy and completeness;
- A verification that samples were properly prepared, preserved and identified;
- A check on field analyses for equipment calibration, and instrument conditions;
- A review of laboratories task orders (if needed) and chain-of-custody forms for proper completion, signatures of field personnel and the laboratory sample custodian, and dates.

9.3.1 Consultant Data Validation

ARCADIS Geraghty & Miller will complete a Level II data validation to verify that the laboratories have performed in accordance with requirements specified in this QAPP and the respective laboratories SOPs (Appendix B). Therefore, the laboratories are required to submit data that are supported by sufficient QC backup information to allow the reviewers to conclusively evaluate the quality of the data.

Validation of analytical data packages will be performed after validation of the field data. Validation will include a systematic review of the data for compliance with the established QC criteria for the methods used, which may be modified as appropriate by the requirements specified in the current U.S. EPA Functional Guidelines for Organics and Inorganics Analyses (U.S. EPA 1994).

Analytical data will be submitted to ARCADIS Geraghty & Miller in hard copy and possibly in a computerized format organized to facilitate data management. The laboratory-provided data flags may include such items as estimated concentration, below required detection limit, and concentration of chemicals also found in blanks. The data reviewer comments will indicate that the data are (1) usable as a quantitative concentration (no data qualifiers present), (2) usable, with caution, as an estimated concentration ("J" or "UJ" data qualifiers present), or (3) unusable due to out-of-control QC results ("R" data qualifiers present). The complete data set will be incorporated into the final evidence file.

10. Performance and Systems Audits

Performance and systems audits for sampling and analysis operations consist of on-site review of field and laboratory QA systems and on-site review of equipment for sampling, calibration, and measurement techniques. Performance and systems audits evaluate and verify that organization, operations, and procedures are in compliance with protocols specified in the QAPP and work plans. Performance and systems audits will be conducted at the discretion of the ARCADIS Geraghty & Miller and/or AK Steel project managers.

11. Preventive Maintenance

11.1 Field Instrument Routine Maintenance Activities

The field instrument routine preventive maintenance procedures for each instrument are specified in the appropriate operation manual.

11.2 Laboratory Instrument Routine Maintenance Activities

The contracted laboratories maintain an equipment maintenance program designed to track routine maintenance, calibration, and repair of laboratory equipment. Maintenance of equipment is in accordance with manufacturer's recommendations and with normal lab practices. Maintenance records are maintained in permanent records or equipment logs.

11.3 Documentation Of Maintenance Activities

All equipment preventive maintenance performed during the project will be noted in field records or on applicable field forms.

11.4 Contingency Plans

All field instruments are pre-tested prior to beginning any fieldwork to determine if instruments are in good working order. To allow for contingencies if an instrument is found to be in need of repair, equipment is also available through other ARCADIS Geraghty & Miller offices or rental companies that may be picked up locally or delivered on short notice by common carrier (e.g., Federal Express).

12. Corrective Action

12.1 Corrective Actions - General Considerations

Corrective actions may be required for two classes of problems: analytical and equipment problems and noncompliance problems. Analytical and equipment problems may occur during sampling, sample handling, sample preparation, laboratory instrumental analysis, and data review. Noncompliance problems occur when activities are conducted outside the requirements of the QAPP. For both types of problems, a formal corrective action program will be implemented at the time the problem is identified. The person who identifies the problem is responsible for notifying the ARCADIS Geraghty & Miller Project Manager who will then contact the project managers of the involved parties, if necessary. If the problem is analytical in nature, information on these problems will be promptly communicated to the appropriate laboratory Project Manager(s).

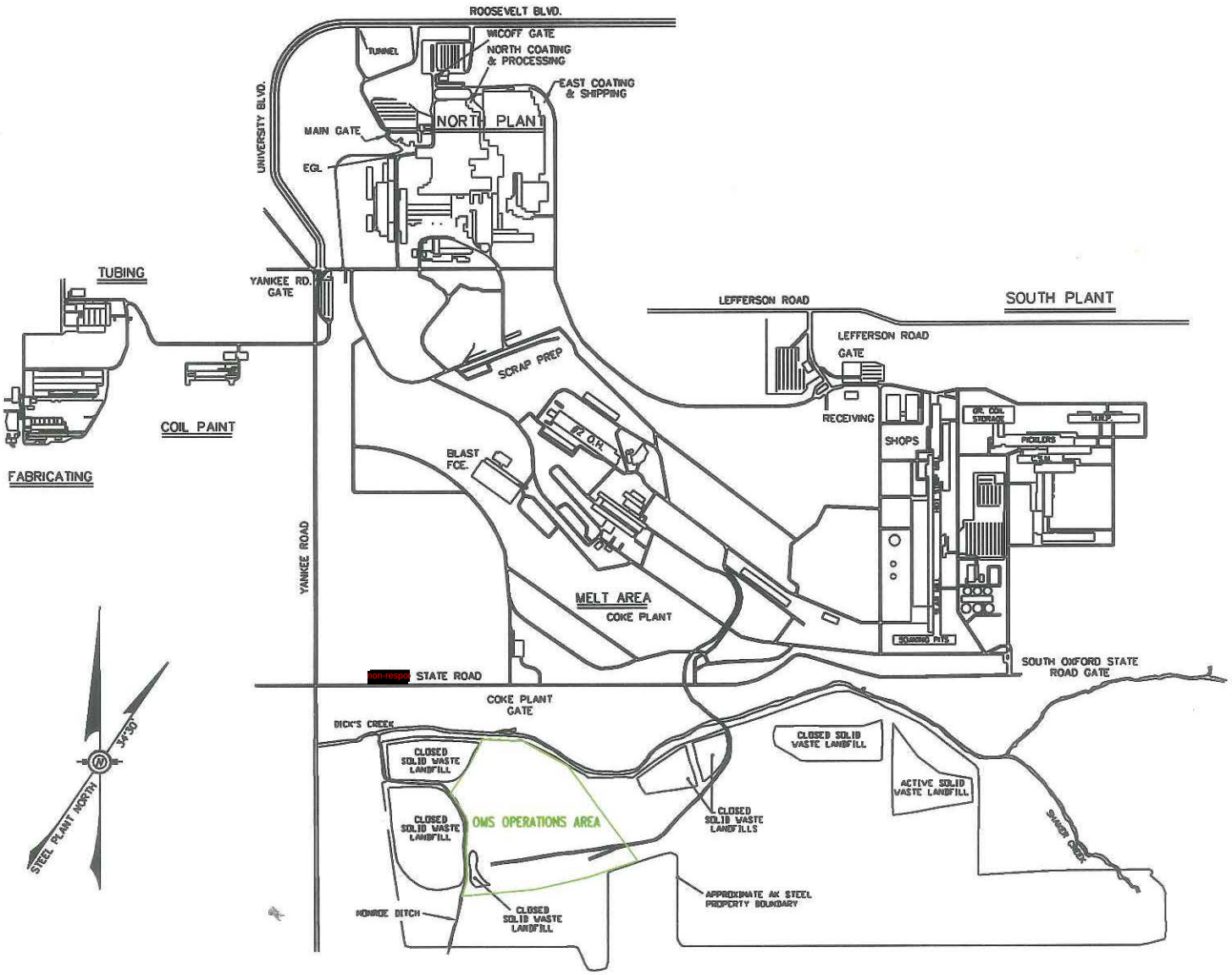
13. Quality Assurance Reports to Management

The laboratory and or field project records will contain a description of the following QA items (if applicable):

- Changes in this QAPP;
- Results of performance evaluation audits;
- Significant QA/QC problems, recommended solutions, and results of corrective actions;
- Data quality assessment in terms of precision, accuracy, representativeness, completeness, comparability and conformance with method detection limits and/or estimated quantitation limits;
- Indication of whether the QA objectives were met; and
- Limitations on use of the measurement data.

The ARCADIS Geraghty & Miller QA Manager will review all aspects of the implementation of this QAPP on a regular basis and prepare summary reports. Reviews will be performed at the completion of each field activity, and summary reports will be completed at this time. A final report will also be prepared at the conclusion of each of the planned investigations.

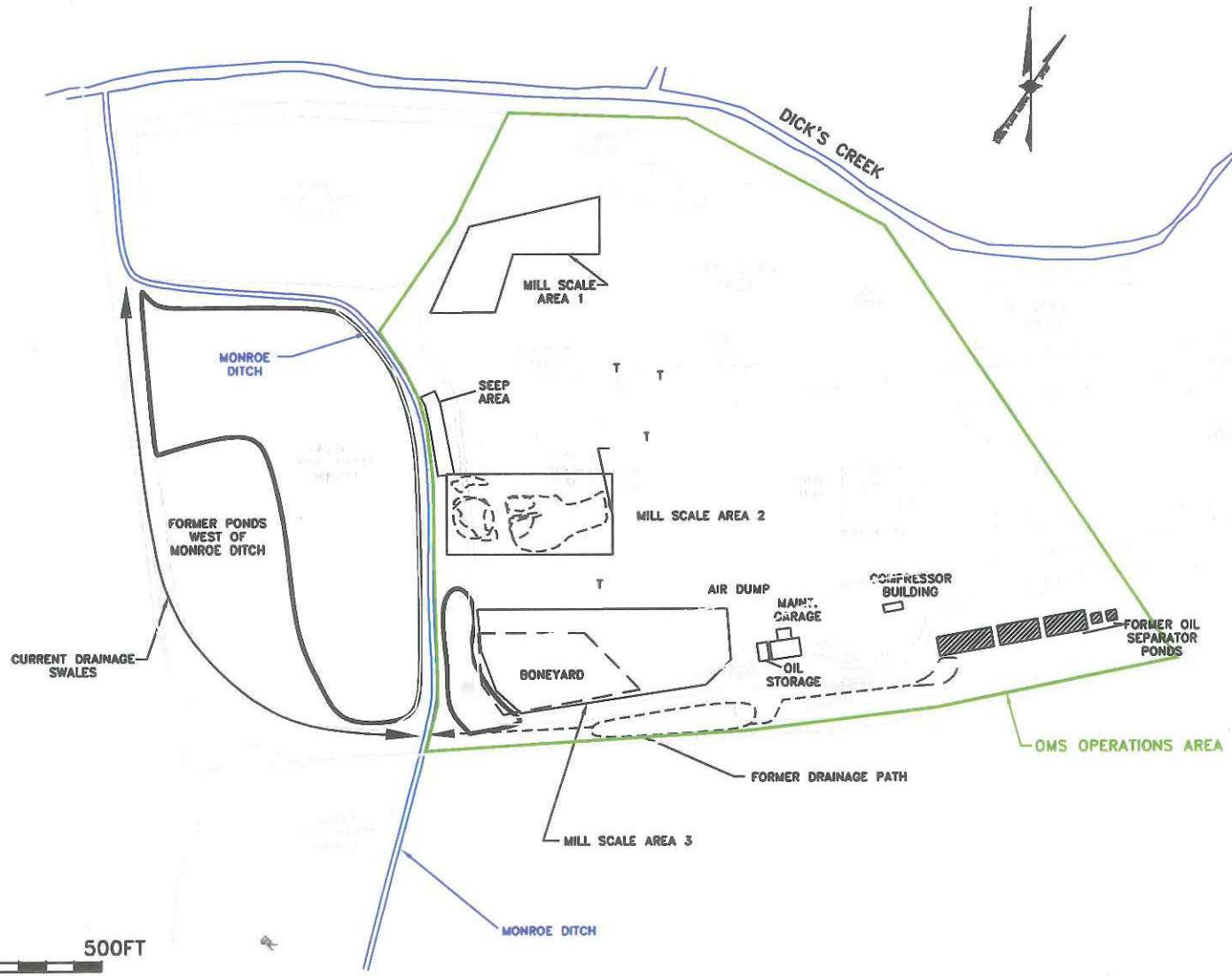
FIGURES



ARCADIS GERAGHTY & MILLER

SITE LOCATION
OMS OPERATIONS AREA,
AK STEEL PROPERTY, MIDDLETOWN, OHIO

DRAWN	DATE	PROJECT MANAGER	DRAWING NAME
R. SMITH	1996	R. ASTLE	AK1
		LEAD DESIGN PROF.	CHECKED
			R. ASTLE
		PROJECT NUMBER	DRAWING NUMBER
		MI000848.009	1



NOTE:

1. AREAS OF INTEREST IDENTIFIED IN BLACK PRINT.

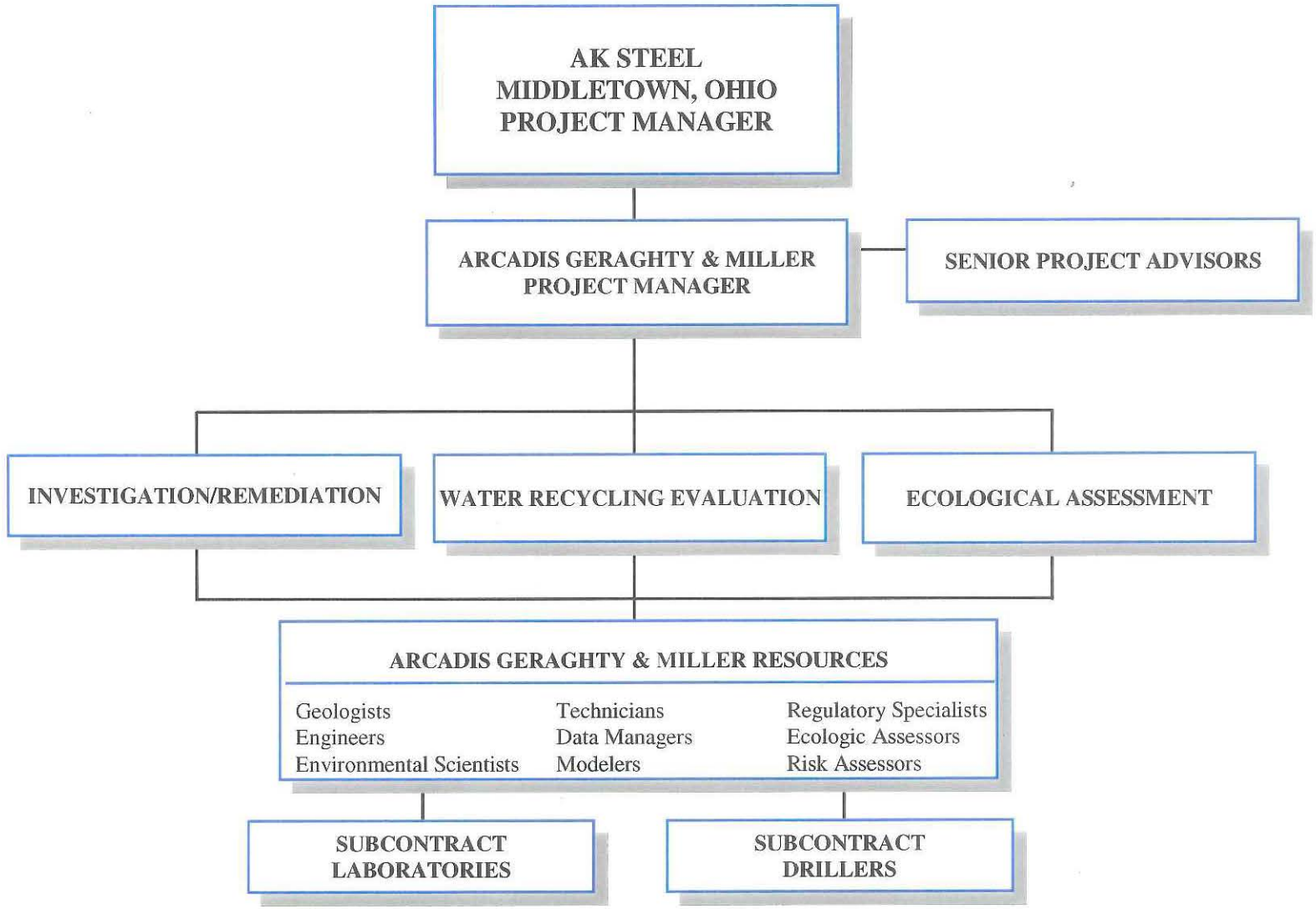
LEGEND

T TRANSFORMER

ARCADIS GERAGHTY & MILLER

SITE LAYOUT, OMS OPERATIONS AREA, AK STEEL PROPERTY, MIDDLETOWN, OHIO

DRAWN	DATE	PROJECT MANAGER	DRAWING NAME
R. SMITH	26FEB00	R. ASTLE	AK\pk2
		LEAD DESIGN PROF.	CHECKED
			R. ASTLE
		PROJECT NUMBER	DRAWING NUMBER
		MI000848.009	2



ARCADIS Geraghty & Miller

Figure 3. ARCADIS Geraghty & Miller Project Organization Chart, OMS Operations Area, AK Steel Corporation, Middletown, Ohio.

Appendix A

Health & Safety Plan

ARCADIS GERAGHTY & MILLER

Health & Safety Plan

Environmental Site
Assessment
Olympic Mills Service
Operations Area
AK Steel Property
Middletown Works
Middletown, Ohio

PREPARED FOR

AK Steel Corporation

1. Site Description

Date(s) of Investigation: To be determined.
Workday duration: 10 hours
Location of Activity: Monroe Ditch Area

Environmental Media Affected by Contamination:
Sediment x Soil x Air Surface Water x Ground Water x

Site Accessibility:
Major Highway Two-Lane Road Dirt Road x

Location of Nearest Population:
Within 1/4 mile Rural Urban x

Topography:
Flat x Sloped (Percent Grade: N/A %)

2. Project Description

This project includes the collection of soil samples, groundwater samples, surface water samples, and sediment samples. Soil samples may be collected using hollow-stem drilling techniques or using a hand auger. Groundwater sampling at the site may be performed using disposable bailers or the use of submersible equipment. Surface water and sediment sampling may involve traversing the drainage channels of Monroe Ditch and Ditch Creek.

3. Organization And Responsibilities

The following personnel are designated to carry out the stated job functions on site:

Project Manager:	Richard Astle
Safety & Health Supervisor:	Mija Coppola
Site Safety & Health Supervisor:	Kevin Patton
Field Personnel:	Kevin Patton/Rebecca Wiesner/Bill Schultz
Sub-Contractors:	Frontz Drilling

All visitors arriving and departing the site should log in and out at the Olympic Mills Service administration trailer and report to the ARCADIS Geraghty & Miller Site Safety & Health Supervisor (SSHS).

5. Hazard Evaluation

Substance(s) known or suspected in environmental media at the site are polychlorinated biphenyls (PCBs). A summary of potential exposure, health effects and physical hazards is presented below.

5.1 Potential Exposure

Principal routes of exposure for PCBs are through ingestion and dermal contact.

5.2 Health Effects

Exposure to PCBs through dermal contact may result in various skin ailments, including chloracne and liver toxicity. Ingestion of PCBs may result in liver toxicity. PCBs are carcinogenic to animals. General symptoms of PCB exposure may include skin and eye irritation and chloracne.

Worker exposure to PCBs will be controlled through the proposed use of personal protective equipment. Eyes should be irrigated immediately if exposure to PCBs is suspected. Skin should be washed immediately if exposure to PCBs is expected. If PCB ingestion is suspected, medical attention should be provided immediately.

5.3 Physical Hazards

The following physical hazards are expected on site:

Overhead Power Lines	(x)	Insects	(x)
Uneven Ground	(x)	Ice	( )
Slippery Conditions	(x)	High Temperatures	(x)
Pinch Points on Rig	(x)	Plant Operations Traffic	(x)
Buried Conduits	( )	Railroad Tracks/Trains	( )
Explosive Atmospheres	( )	Vegetation (Poison Ivy)	(x)

6. Site Evaluation

Portions of the site may have various types of equipment and trip hazards that should be avoided to prevent injury. The proximity to mobile equipment demands attention. Some steep slopes and/or drainage ditch areas may pose a hazard. Loose stone or slag can cause slip, trip or fall hazards.

7. Personal Protective Equipment

The following levels of personal protection have been designated for the corresponding work tasks:

Location/Job Function	Levels of Protection
Soil, Sediment, Surface Water And Groundwater Sampling	Level D

Specific protective equipment for each level of protection is presented below:

- Level D:
  - Chemical-resistant clothing (one-piece Tyvek coverall, requirement for hood to be determined; Saranex coveralls). Selection of garment is to be based upon site conditions and work task.
  - Gloves; outer (Neoprene).
  - Gloves; inner (skin-tight Latex).
  - Boots; chemical resistant to substances of concern, steel toe and metatarsal protection.
  - Hardhat (face shield optional).
  - Safety glasses with side shields.
  - Long sleeved shirts, sleeves will be taped to gloves, and cuffs taped to boots, as applicable.
  - No finger rings.

8. Environmental Monitoring

Environmental conditions will be monitored during site investigation field activities to determine the proper level of personal protection and to determine if any response actions are necessary. Air monitoring for volatile organic compounds (VOCs) will be performed at shoulder height (in the breathing zone) of those workers most likely to be exposed to potentially hazardous concentrations of contaminants in the vicinity of field activities, if conditions warrant during subsurface soil sampling (drilling activities).

9. Safe Work Practices And Special Procedures

The following practices will be strictly adhered to by personnel, and as enforced by the SSHS:

- Absolutely no smoking and/or eating and drinking will be allowed on-site except in designated areas;
- Personnel will adhere to safe practices as presented in the AK Steel health and safety training and daily health and safety meetings.

10. Emergency Planning

10.1 On-Site Responsibility

The SSHS is responsible for the implementation of this plan. If organic vapors or other adverse conditions are detected during drilling, work will be discontinued and the site evacuated by the SSHS. The field investigation program may then be modified to include VOC monitoring or other controls as needed.

Should accident or fire occur, contact emergency personnel immediately and then contact the ARCADIS Geraghty & Miller Safety & Health Supervisor.

10.2 Emergency Care

Hospital: Middletown Hospital, 105 McNight Drive, Middletown, OH, 45024.

Local ambulance, fire, and police service is available from Middletown using the 911 emergency service phone number.

First-aid equipment is available at the following locations:

First-Aid Kit: SSHS's Vehicle

Eye-Wash Kit: SSHS's Vehicle

List of emergency phone numbers:
Police: 911
Fire: 911
Hospital: (513) 424-2111

11. Recordkeeping

The following documentation will be maintained and updated by the ARCADIS Geraghty & Miller SSHS:

- Safety and Health Logbook, and forms therein.

Prior to program startup, a safety briefing will be conducted by the SSHS covering potential hazards and contents of this Plan.

12. Signatures

Project No.: MI000848.0001,2,3,4,5,6,7

Project Name & Location: Phase II Environmental Site Assessment, Monroe Ditch Area, AK Steel Property, Middletown, Ohio

The undersigned have read and understand the site health and safety plan for the Phase II Environmental Site Assessment, Monroe Ditch Area, AK Steel Property, Middletown, Ohio.

Name	Signature	Date
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

Site Safety and Health Supervisor:

Kevin Patton	_____	_____